THE QUANTUM MECHANICAL KINETIC THEORY OF LOADED SPHERES *

by

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ABSTRACT

The transport coefficients of a gas of loaded spheres, that is, spheres in which the center of mass does not coincide with the geometrical center are considered. The amount by which the center of mass is displaced from the center of the sphere is denoted by δ and the diameter of the sphere is σ. The scattering amplitude and cross section are found as power series in δ/σ; the coefficients of the zero, first, and second power of δ/σ are obtained. Using these results, the quantum mechanical expressions for the relaxation time, coefficient of shear viscosity, and coefficient of thermal conductivity are also obtained explicitly to second order in δ/σ. These quantities are then evaluated, numerically, in the limit that Planck's constant approaches zero. The results are found to agree with results obtained by purely classical methods.

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CHAPTER I

INTRODUCTION

Statistical mechanics is that field of physics which attempts to predict the properties and behavior of an aggregate of a large number of particles, when the laws governing the interaction of the constituent particles are known. This field is divided into two branches -- equilibrium statistical mechanics, by means of which such properties of a substance at equilibrium as the energy, heat capacity, and equation of state are determined; and non-equilibrium statistical mechanics, which has as its central problem the determination of the transport properties of systems, usually gases.

Although speculations on the atomic structure of matter date back to the ancient Greeks, a mathematically rigorous attack upon the problems of the kinetic theory of gases was not made until the middle of the nineteenth century. J. C. Maxwell[1] in 1866 derived the equations of change for a non-uniform gas. L. Boltzmann[2] in 1872 established his H-theorem, and published the integro-differential equation which bears his name. Attempts to solve this equation met with small success until 1916-1917 when S. Chapman[3] and D. Enskog[4] independently published their solutions of Boltzmann's equation. An extensive discussion of this solution is given by Chapman and Cowling[5], and by

Hirschfelder, Curtiss, and Bird[6]. This solution, and the Boltzmann equation itself, is based on the following assumptions:

1. Classical mechanics is valid to describe molecular interactions.

2. The gas is sufficiently dilute that three body collisions may be ignored.

3. The molecules have no internal structure; they are point particles surrounded by spherically symmetric fields of force.

Research in kinetic theory since the time of Chapman and Enskog has been principally directed toward the removal of these restrictions.

Successful attempts to introduce quantum mechanics into kinetic theory were first made by E. Uehling and G. Uhlenbeck.[7] They presented a modified form of the Boltzmann equation in which both statistics effects, arising from the Pauli exclusion principle, and diffraction effects, arising from the wave nature of matter, are taken into account. Quantum mechanically it is impossible to say that a particle with a given energy and angular momentum will be scattered through a definite angle upon collision with another particle. This results in the classical cross section being replaced by its quantum analog in the Boltzmann collision integral. An extensive discussion of these matters is given by Hirschfelder, Curtiss, and Bird[8], and by Mori, Oppenheim, and Ross[9].

Attempts to extend the treatment to dense gases were first made by Enskog[10] himself, who in 1922 formulated a modification of the Boltzmann equation for a dense gas of rigid spheres. Many contributions along this line have been made by subsequent workers.

The kinetic theory of molecules with internal degrees of freedom was considered from the mean free path approach by J. Jeans[11,12]. He derived an expression for the rate of equilibration of rotational and translational kinetic energy for a gas of loaded spheres, that is, spheres in which the center of mass is slightly displaced from the geometrical center. The first successful attempt to apply the Chapman-Enskog method to a molecule with internal degrees of freedom was made by Pidduck[13], who determined the transport coefficients for a gas of perfectly rough spheres. A more exact treatment of the loaded sphere has been given in a series of two papers by Dahler and Sather[14], and Sandler and Dahler[15], and of the rough sphere by Condiff, Lu, and Dahler[16]. An extensive treatment of the kinetic theory of smooth rigid ovaloids has been given by Curtiss[17]. He derived a Boltzmann equation appropriate to these molecules, and gave a solution in terms of certain integral expressions. These were then evaluated for the special case of the spherocylinder, that is, a cylinder with hemispherical caps[18]. Kagan and Afanas'ev[19] pointed out that terms in the expansion of the perturbation function arising from coupling between the linear and angular velocities were ignored in this treatment. The effect of these added terms was considered in the work on the rough sphere and loaded sphere mentioned above.

The work thus far mentioned has dealt with the removal of some one of the restrictive assumptions. In this thesis, however, we deal with a quantum mechanical system of molecules with internal degrees of freedom. In the following section we present certain results pertinent to this work.

Section 1.1 The Transport Coefficients of a Quantum Gas with Internal Degrees of Freedom

Expressions for the transport coefficients of a gas with internal states based upon quantum mechanics were first derived by Wang Chang, Uhlenbeck, and de Boer[20,21]. They introduce a distribution function $f_i(\underline{r},\underline{v},t)$, which is a function of the position, velocity, time, and quantum number i specifying the internal state of the molecule. The number of molecules with internal state specified by the quantum number i which at time t lie in an element $d\underline{r}\,d\underline{v}$ about $\underline{r},\underline{v}$ is $f_i(\underline{r},\underline{v},t)\,d\underline{r}\,d\underline{v}$. The Boltzmann equation which they then write for $f_i(\underline{r},\underline{v},t)$ is

$$\frac{\partial f_i}{\partial t} + \underline{v} \cdot \frac{\partial f_i}{\partial \underline{r}} + \frac{1}{m} \underline{F} \cdot \frac{\partial f_i}{\partial \underline{v}} = \sum_{jkl} \int (f_k' f_{1l}' - f_i f_{1j}) g \, I_{ij}^{kl}(g, \chi, \varphi) \sin \chi \, d\chi \, d\varphi \, d\underline{v}_1 \, . \tag{1.1-1}$$

The quantity $I_{ij}^{kl}(g, \chi, \varphi)$ is the cross section for the scattering of particles in states i and j with relative velocity g to states k and l with relative velocity g'. The angles χ and φ are the polar angles of g' with respect to g. The primes on the distribution functions indicate that they are functions of post-collision velocities. Wang Chang, Uhlenbeck, and de Boer solve this equation in a manner similar to the classic Chapman-Enskog method. The results which they obtain for the transport coefficients are given in Chapter VI of this thesis. This quantum mechanical treatment of molecules with internal structure has been generalized to the treatment of mixtures by Snider[22].

The treatment of this problem by Wang Chang, Uhlenbeck, and de Boer is not completely satisfactory, however, since the translational motion of the molecules is treated classically, and the internal states are assumed to be non-degenerate. Also, the Boltzmann equation with which they begin, Eq. 1.1-1, is not obtained in a rigorous derivation.

More rigorous derivations of the Boltzmann equation for a quantum gas with internal degrees of freedom were given independently by Waldmann[23] and Snider[24]. Snider's derivation begins with the quantum analog of the Liouville equation, and makes use of the formal scattering theory of Lippmann and Schwinger. In a recent paper McCourt and Snider[25] have solved this equation to obtain the coefficient of thermal conductivity for a gas with rotational degrees of freedom. For a gas in which the local angular momentum density is zero, their results are essentially the same as those of Wang Chang, Uhlenbeck, and de Boer, except that added terms, corresponding to those discussed by Kagan and Afanas'ev, are included. Except for these added terms, the only difference is that the cross section introduced by Wang Chang, Uhlenbeck, and de Boer is replaced by the true cross section, averaged over the degenerate internal states.

Snider[22] obtained expressions for the collision cross section of rigid spheres being scattered from rigid spheroids of small eccentricity. This led to an expression for the coefficient of diffusion which was evaluated explicitly in the low temperature region where quantum effects are large. In this thesis we treat the model of the loaded sphere. Since their centers of mass do not coincide with their geometrical centers, loaded spheres wobble during their motion. Upon collision they can exchange translational and rotational kinetic energy. It is for this reason that the model is of interest. Our goal is to use the formulas of Wang Chang, Uhlenbeck, and de Boer, as interpreted by McCourt and Snider (neglecting the added terms of Kagan and Afanas'ev), to obtain expressions for the transport coefficients for a gas of loaded spheres. In order to accomplish this, we must first obtain an expression for the collision cross section. This we do using the results of Gioumousis and Curtiss on the scattering of diatomic molecules.

Section 1.2 The Scattering of Diatomic Molecules

Let us first consider a beam of point particles, moving in the positive z direction, being scattered by a center of force. If the incoming particles all have momentum $\underline{p} = \hbar \underline{\kappa}$, the asymptotic form of the wavefunction is

$$\psi \sim e^{i\kappa z} + f(\vartheta,\varphi)\, r^{-1} e^{i\kappa r} . \qquad (1.2\text{-}1)$$

Here $\underline{\kappa}$ is the propagation vector, and the quantity $f(\vartheta,\varphi)$ is called the scattering amplitude. By using this wavefunction to calculate the current density far away from the scattering center, it can be shown that the probability that a given incident particle will be scattered into a unit solid angle about ϑ, φ is equal to $|f(\vartheta,\varphi)|^2$. Hence we define the scattering cross section $I(\vartheta,\varphi)$ by the equation

$$I(\vartheta,\varphi) = |f(\vartheta,\varphi)|^2 . \tag{1.2-2}$$

In order to treat the collision of loaded spheres we need the generalization of the above results to the case where the molecules have internal degrees of freedom. In a series of three papers Gioumousis and Curtiss[26-28] have developed an extensive treatment of the theory of diatomic molecular collisions. This theory is appropriate to the loaded sphere case, since a loaded sphere may be imagined as a diatomic molecule with a rigid spherical potential surrounding it.

The internal state of a diatomic molecule is specified by giving two quantum numbers--ℓ, which specifies the energy, and m, which specifies the z component of the angular momentum. The molecules are considered as rigid rotators, so that no vibrational degree of freedom is present. The energy E_ℓ corresponding to the quantum number ℓ is given by

$$E_\ell = \frac{\hbar^2 \ell(\ell+1)}{2\Gamma K T} , \tag{1.2-3}$$

where Γ is the moment of inertia about an axis through the center of mass perpendicular to the symmetry axis, K is Boltzmann's constant, and T is the absolute temperature.

Let us consider two such molecules, molecule a with internal quantum numbers ℓ^a and m^a, and molecule b, with internal quantum numbers ℓ^b and m^b. The Hamiltonian $\mathcal{H}$ for this system is given by

$$\mathcal{H} = -\frac{\hbar^2}{2\mu}\frac{\partial}{\partial \underline{r}}\cdot\frac{\partial}{\partial \underline{r}} + \mathcal{H}_{int}^{a} + \mathcal{H}_{int}^{b} + V , \tag{1.2-4}$$

where $\underline{r}$ is the vector from the center of mass of molecule b to that of a, μ is the reduced mass of the pair, $\mathcal{H}_{int}^{a}$ and $\mathcal{H}_{int}^{b}$ are the internal Hamiltonians for molecules a and b, and V is the intermolecular potential. The term referring to the motion of the center of mass of the system as a whole has been removed from the Hamiltonian.

Let $S_{\ell^a m^a}(\vartheta^a, \varphi^a)$ be an eigenfunction of $\mathcal{H}_{int}^{a}$ corresponding to internal energy E_{ℓ^a}, that is,

$$\mathcal{H}_{int}^{a}\, S_{\ell^a m^a}(\vartheta^a, \varphi^a) = E_{\ell^a}\, S_{\ell^a m^a}(\vartheta^a, \varphi^a) . \tag{1.2-5}$$

Then, as is shown by Gioumousis and Curtiss, the asymptotic form of the wavefunction, corresponding to the molecules having initial relative momentum $\underline{p} = \hbar\, \underline{\mathcal{K}}_{\bar{\ell}^a \bar{\ell}^b}$, and initial internal states specified by quantum numbers $\bar{\ell}^a$, $\bar{m}^a$ and $\bar{\ell}^b$, $\bar{m}^b$, is

$$\psi \sim e^{i \varkappa_{\bar{\ell}^a \bar{\ell}^b} \cdot \underline{r}} S_{\bar{\ell}^a \bar{m}^a}(\vartheta^a, \varphi^a) S_{\bar{\ell}^b \bar{m}^b}(\vartheta^b, \varphi^b)$$

$$+ \sum_{\ell^a m^a \ell^b m^b} f(\bar{\ell}^a \bar{m}^a \bar{\ell}^b \bar{m}^b, \ell^a m^a \ell^b m^b) r^{-1} e^{i \varkappa_{\ell^a \ell^b} r}$$

$$\times S_{\ell^a m^a}(\vartheta^a, \varphi^a) S_{\ell^b m^b}(\vartheta^b, \varphi^b) . \qquad (1.2\text{-}6)$$

The wave number $\varkappa_{\ell^a \ell^b}$ is given by the equation of conservation of energy

$$\frac{\hbar^2 \varkappa^2_{\bar{\ell}^a \bar{\ell}^b}}{2\mu} + E_{\bar{\ell}^a} + E_{\bar{\ell}^b} = \frac{\hbar^2 \varkappa^2_{\ell^a \ell^b}}{2\mu} + E_{\ell^a} + E_{\ell^b} . \qquad (1.2\text{-}7)$$

Then, corresponding to Eq. 1.2-2 for point particles, the cross section for scattering from states $\bar{\ell}^a \bar{m}^a \bar{\ell}^b \bar{m}^b$ to states $\ell^a m^a \ell^b m^b$ is given by

$$I(\bar{\ell}^a \bar{m}^a \bar{\ell}^b \bar{m}^b, \ell^a m^a \ell^b m^b) = \frac{\varkappa_{\ell^a \ell^b}}{\varkappa_{\bar{\ell}^a \bar{\ell}^b}} \left| f(\bar{\ell}^a \bar{m}^a \bar{\ell}^b \bar{m}^b, \ell^a m^a \ell^b m^b) \right|^2 .$$

$$(1.2\text{-}8)$$

A rigorous treatment shows that the scattering amplitude and the cross section are, in general, functions of both the incoming direction T and the outgoing direction R. This is due to the degeneracy of the internal states, and the necessity of choosing a direction fixed in space for the quantization of these states. Gioumousis and Curtiss expand this cross section in an infinite series:

$$I(T|\bar{\ell}^a\bar{m}^a\bar{\ell}^b\bar{m}^b, \ell^a m^a \ell^b m^b|R)$$

$$= \sum_{\lambda_3\lambda_4\mu_4} I(\bar{\ell}^a\bar{m}^a\bar{\ell}^b\bar{m}^b|\lambda_3\lambda_4\mu_4|\ell^a m^a \ell^b m^b)$$

$$\times D^{\lambda_3}(T)_{0,-\mu_4} D^{\lambda_4}(R)_{0\mu_4}. \qquad (1.2\text{-}9)$$

The quantities $D^\lambda(R)_{mn}$ appearing in this expression are the representation coefficients of the three dimensional rotation group, and R is a matrix which specifies a direction in space. The manner in which a matrix is associated with a direction in space will be explained in detail in Chapter II for the special case of the loaded sphere.

An explicit expression for the coefficient $I(\bar{\ell}^a\bar{m}^a\bar{\ell}^b\bar{m}^b|\lambda_3\lambda_4\mu_4|\ell^a m^a \ell^b m^b)$ appearing in Eq. 1.2-9 has been given by Gioumousis and Curtiss. It contains several Wigner, or Clebsch-Gordan, coefficients, $S^{l^a l^b}_{l m^a m^b}$, some properties of which are given in Appendix I. It also contains a quantity $f(\bar{l}^a \bar{l}^b \bar{l} \bar{\lambda} L l^a l^b l \lambda)$; it is this quantity which is determined for any particular molecular model before the cross section itself is evaluated. We shall refer to $f(\bar{l}^a \bar{l}^b \bar{l} \bar{\lambda} L l^a l^b l \lambda)$ as the scattering amplitude; this is in a sense a misnomer, since the real scattering amplitude is the quantity $f(\bar{l}^a \bar{m}^a \bar{l}^b \bar{m}^b, l^a m^a l^b m^b)$ of Eq. 1.2-6. In order to abbreviate the notation the symbol p is introduced to stand for the four summation indices $l^a l^b l \lambda$. The scattering amplitude may then be written simply as $f(\bar{p} L p)$.

For collisions of two rigid bodies the scattering amplitude $f(\bar{p} L p)$ is found in the following way. The wavefunction for the system corresponding to configurations in which the two bodies do not overlap can be written down. A function $\rho(S^a, S^b)$, called the distance of closest approach function, is now introduced. It is defined to be the distance between the centers of mass of the molecules when molecule a with orientation S^a touches molecule b with orientation S^b . Since the bodies are rigid the wavefunction must be zero for a configuration of the two bodies in which they overlap, and hence must, by continuity, be zero for any configuration in which they just touch. It is shown by Gioumousis and Curtiss that this leads to the following boundary condition:

$$0 = \sum_{l^a l^b l \lambda s} \left[\delta_{p\bar{p}}\, j_{\bar{\lambda}}\left(\bar{\mathcal{H}} \rho(S^a, S^b)\right) + \mathcal{H} i^{\lambda+1} f(\bar{p} L p)\, h_{\lambda}\left(\mathcal{H} \rho(S^a, S^b)\right) \right]$$

$$\times\, S^{l^a l^b}_{l s \tau - s}\, S^{l \lambda}_{L \tau 0}\, D^{l^a}(S^a)_{0 s}\, D^{l^b}(S^b)_{0\, \tau - s} ,$$

(1.2-10)

where j_λ and h_λ are the spherical Bessel and Hankel functions, $\mathcal{H}$ equals $\mathcal{H}_{l l^a l^b}$, and $\bar{\mathcal{H}}$ equals $\mathcal{H}_{\bar{l} l^a \bar{l}^b}$.

If the distance of closest approach function is known, the above equation may in principle be solved for $f(\bar{p} L p)$. Then, the coefficients in the expansion of the cross section may be evaluated by means of the following formula[27]:

$$I(\bar{l}^a \bar{m}^a \bar{l}^b \bar{m}^b | \lambda_3 \lambda_4 \mu_4 | l^a m^a l^b m^b) = \frac{\mathcal{H}}{\hbar} \frac{(2\bar{l}^a+1)(2\bar{l}^b+1)}{(2l^a+1)(2l^b+1)}$$

$$\times \sum_{\substack{\bar{l} l \bar{\lambda} \lambda \bar{l}' l' \\ \bar{\lambda}' \lambda' L L' \mu_3}} i^{\bar{\lambda}-\bar{\lambda}'} (-1)^{\mu_4} (2\bar{\lambda}'+1)(2\bar{\lambda}+1)\, S^{\bar{l}\bar{\lambda}}_{L \bar{m} \mu_3-\bar{m}}$$

$$\times (-1)^{m+\bar{m}}\, S^{\bar{l}'\bar{\lambda}'}_{L' \bar{m} \mu_3-\mu_4-\bar{m}}\, S^{l\lambda}_{L m \mu_3-m}\, S^{l'\lambda'}_{L' m \mu_3-\mu_4-m}\, S^{\bar{l}^a \bar{l}^b}_{\bar{l} \bar{m}^a \bar{m}^b}$$

$$\times S^{\bar{l}^a \bar{l}^b}_{\bar{l}' \bar{m}^a \bar{m}^b}\, S^{l^a l^b}_{l m^a m^b}\, S^{l^a l^b}_{l' m^a m^b}\, S^{\bar{\lambda}\bar{\lambda}'}_{\lambda_3 0 0}\, S^{\lambda\lambda'}_{\lambda_4 0 0}$$

$$\times S^{\bar{\lambda}\bar{\lambda}'}_{\lambda_3\, \bar{m}-\mu_3,\, \mu_3-\mu_4-\bar{m}}\, S^{\lambda\lambda'}_{\lambda_4\, \mu_3-m,\, m+\mu_4-\mu_3}\, f(\bar{l}^a \bar{l}^b \bar{l} \bar{\lambda} L l^a l^b l \lambda)$$

$$\times f(\bar{l}^a \bar{l}^b \bar{l}' \bar{\lambda}' L' l^a l^b l' \lambda')^* . \tag{1.2-11}$$

We now have in principle a method for calculating the transport coefficients quantum mechanically for a gas of rigid bodies. We can determine the scattering amplitude from Eq. 1.2-10. Eq. 1.2-11 then yields the cross section expansion coefficients. Finally, the transport coefficients are obtained from the formulas given by Wang Chang, Uhlenbeck, and de Boer.

This is the program which will be carried out in this thesis for the loaded sphere. The distance of closest approach function and the scattering amplitude are determined in Chapter II. Then in Chapter III the cross section (actually, a cross section averaged over the degenerate internal states) is found. We define δ to be the displacement of the center of mass of the loaded sphere from the geometrical center and σ to be the diameter of the sphere, and obtain the cross section in the form of a power series in δ/σ. The coefficient of the zero order term is just the cross section for rigid spheres, and the coefficient of the first power of δ/σ is zero. We evaluate exactly the coefficient of the second power of δ/σ. Thus our results are valid only for small values of this parameter. Except for Snider's results, in which one molecule is taken to be spherical, we believe that this is the first exact evaluation of the quantum mechanical cross section for all transitions of a molecule with internal degrees of freedom.

In Chapter IV certain moments of this cross section are calculated which are analogous to the $Q^{(1)}$ and $Q^{(2)}$ of the classical kinetic theory. By using these quantities, along with the formulas of Wang Chang, Uhlenbeck, and de Boer for the transport coefficients, one could calculate exactly the quantum transport coefficients for a gas of loaded spheres, valid for small δ/σ.

As a check upon the results obtained, and in order to be able to estimate the importance of various terms in the expressions for the transport coefficients, we then, in Chapter V, obtain expansions of the moments obtained in Chapter IV in power series in Planck's constant. Finally, in Chapter VI, we use these expansions to obtain the classical limit of the transport coefficients. The results thus obtained are in agreement with the results which Sandler and Dahler[15] obtained by purely classical methods.

CHAPTER II

THE SCATTERING AMPLITUDE

In Chapter I the work of Gioumousis and Curtiss on the scattering of diatomic molecules was discussed in general, with particular emphasis on the scattering of rigid bodies. It was shown there how the cross section is evaluated when the asymptotic part of the wave function, or the scattering amplitude, is known. It was further shown there how the scattering amplitude is determined from the condition that the wavefunction be zero for any configuration of the bodies in which they overlap. In this chapter we obtain an expression for the scattering amplitude for the loaded sphere model as a power series in the parameter δ/σ, which is a measure of the degree to which the loaded sphere under consideration differs from an ordinary rigid sphere.

Section 2.1 The Geometry of the Loaded Sphere

The model with which this thesis deals is the loaded sphere. This is a sphere in which the center of mass does not coincide with the geometrical center. Let $\underline{\mathcal{r}}$ be the vector from the origin of space-fixed coordinate axes to the center of mass of the sphere, $\underline{\delta}$ the vector from the center of mass to the geometrical center, and σ the diameter. We wish to find a set of coordinates suitable for the specification of the orientation of the sphere. One set which we could use would be the polar angles ϑ and φ of the vector $\underline{\delta}$. This is essentially what will be done, but in order that we may use the notation of group theory we adopt the following scheme. Let a set of coordinate axes X', Y', Z' be embedded in the sphere, with the origin O' at the center of mass, and the Z' axis directed along $\underline{\delta}$. The Z' axis is therefore an axis of symmetry. Then, by specifying the vector $\underline{r}$ and the three Eulerian angles[29] α, β, and γ of the primed axes with respect to the unprimed, we completely specify the position and orientation of the sphere. The first two angles α and β are just the polar angles of the vector $\underline{\delta}$. Due to the symmetry of the sphere the third Eulerian angle is arbitrary.

With each orientation of the sphere we associate a matrix S defined by

$$S = \begin{pmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix} \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (2.1\text{-}1)$$

Viewed as a matrix which rotates vectors this matrix has the following effect. Let $\hat{u} = (\sin\beta\cos\alpha, \sin\beta\sin\alpha, \cos\beta)$ be a unit vector whose polar angles ϑ and φ are β and α. Then

$$S \cdot \hat{u} = (0,0,1). \tag{2.1-2}$$

Thus the matrix S rotates this vector into coalignment with the Z axis. Alternatively, we may view S as the matrix linking the coordinates of the same point in the two coordinate systems. If $\underline{r}$ = (x,y,z) are the coordinates of a point in the space-fixed system, and $\underline{r}'$ = (x', y', z') the coordinates of the <u>same point</u> in the body-fixed system, then

$$\underline{r}' = S \cdot \underline{r}. \tag{2.1-3}$$

Thus we may specify the orientation of a molecule by giving the associated matrix S.

Section 2.2 <u>The Distance of Closest Approach Function</u>

Consider now a pair of loaded sphere molecules labelled a and b. Let $\underline{r}^a$ be the vector from the origin to the center of mass of a, $\underline{r}^b$ the corresponding vector for molecule b, and $\underline{r} = \underline{r}^a - \underline{r}^b$.

The orientations of the molecules are specified by the rotation matrices S^a and S^b in the manner just described. Then for two spheres in contact (Fig. 1) we may define a function $\rho(S^a, S^b)$ by the equation

$$\rho(S^a, S^b) = |\underline{r}|. \tag{2.2-1}$$

This function $\rho(S^a, S^b)$ is called the distance of closest approach function. It is clearly a function only of the relative orientation of the molecules, and is invariant to a rotation of the system as a whole. We may therefore choose the Z axis to be in the direction of the vector $\underline{r}$, and may choose the first Eulerian angle of S^a equal to zero. Hence the vector $\underline{\delta}^a$ lies in the X-Z plane on the positive side of the X axis. The third Eulerian angle of both S^a and S^b is arbitrary and can be taken to be zero.

With these conventions we have

$$\underline{\delta}^a = \delta(\sin\beta^a, 0, \cos\beta^a), \tag{2.2-2}$$

$$\underline{\delta}^b = \delta(\sin\beta^b\cos\alpha^b, \sin\beta^b\sin\alpha^b, \cos\beta^b), \tag{2.2-3}$$

and

$$\underline{r} = r(0, 0, 1), \tag{2.2-4}$$

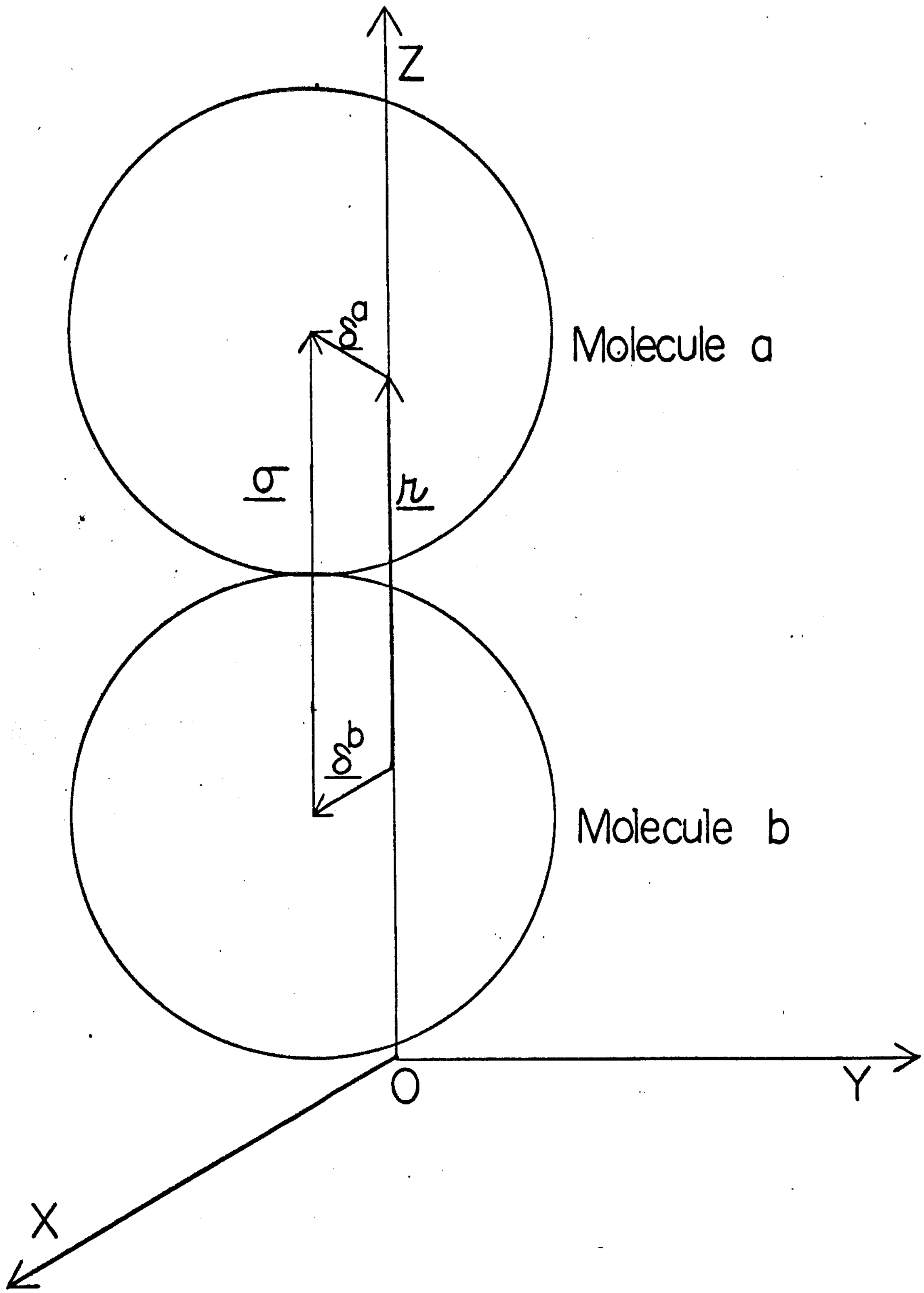
Z
$\underline{\delta}^a$
Molecule a
$\underline{\sigma}$
$\underline{r}$
$\underline{\delta}^b$
Molecule b
O
Y
X

Fig. 1

where we have set $|\underline{\delta}^a| = |\underline{\delta}^b| = \delta$. Further let

$$\underline{\sigma} = \underline{r} + \underline{\delta}^a - \underline{\delta}^b. \tag{2.2-5}$$

Then

$$\sigma^2 = |\underline{\sigma}|^2 = |\underline{r} + \underline{\delta}^a - \underline{\delta}^b|^2$$

$$= \delta^2 (\sin\beta^a - \sin\beta^b \cos\alpha^b)^2$$

$$+ \delta^2 (\sin\beta^b \sin\alpha^b)^2 + [\rho(S^a, S^b) + \delta(\cos\beta^a - \cos\beta^b)]^2. \tag{2.2-6}$$

We now obtain an expression for $\rho(S^a, S^b)$ as a power series in δ/σ. For reasons which will become clear later, we retain terms through second order in δ/σ . From Eq. 2.2-6 we find that

$$\rho(S^a, S^b) = \sigma - \delta(\cos\beta^a - \cos\beta^b)$$

$$- \frac{\delta^2}{2\sigma}(\sin^2\beta^a - 2\sin\beta^a \sin\beta^b \cos\alpha^b + \sin^2\beta^b) + \cdots. \tag{2.2-7}$$

It is convenient at this point to introduce the representation coefficients of the three dimensional rotation group[30]

$$D^{\ell}(S)_{0m} = \sqrt{\frac{4\pi}{2\ell+1}} \; Y_{\ell}^{m}(\beta,\alpha)$$

$$= i^{|m|-m} \sqrt{\frac{(\ell-|m|)!}{(\ell+|m|)!}} \; P_{\ell}^{m}(\cos\beta) e^{im\alpha} , \tag{2.2-8}$$

and to write $\rho(S^a, S^b)$ in the following form:

$$\rho(S^a, S^b) = \rho_0 + \left(\frac{\delta}{\sigma}\right) \rho_1(S^a, S^b)$$

$$+ \left(\frac{\delta}{\sigma}\right)^2 \rho_2(S^a, S^b) + \cdots , \tag{2.2-9}$$

where

$$\rho_0 = \sigma , \tag{2.2-10}$$

$$\rho_1 = \sigma \left[D^1(S^b)_{00} - D^1(S^a)_{00} \right] , \tag{2.2-11}$$

and

$$\rho_2 = \sigma \Big[-\tfrac{2}{3} + \tfrac{1}{3} D^2 (S^a)_{00}$$

$$- D^1(S^a)_{0-1} D^1(S^b)_{01} - D^1(S^a)_{01} D^1(S^b)_{0-1} + \tfrac{1}{3} D^2(S^b)_{00} \Big].$$

(2.2-12)

We now use these results to obtain the scattering amplitude for the collision of two loaded spheres.

Section 2.3 <u>The Expansion of the Scattering Amplitude in Powers of δ/σ</u>

The condition that the wavefunction be zero when the spheres touch leads to the boundary condition given by Eq. 1.2-10 where, it will be remembered, p stands for the four quantum numbers ℓ^a, ℓ^b, ℓ, and λ. Upon introducing the expansion of ρ, Eq. 2.2-9, into the abovementioned equation, Eq. 1.2-10, and using the expansions

$$j_{\bar{\lambda}}(\bar{\varkappa}\rho) = j_{\bar{\lambda}}(\bar{\varkappa}\sigma) + \left(\frac{\delta}{\sigma}\right) \bar{\varkappa}\rho_1 j_{\bar{\lambda}}'(\bar{\varkappa}\sigma)$$

$$+ \left(\frac{\delta}{\sigma}\right)^2 \left[\bar{\varkappa}\rho_2 j_{\bar{\lambda}}'(\bar{\varkappa}\sigma) + \frac{1}{2}\bar{\varkappa}^2 \rho_1^2 j_{\bar{\lambda}}''(\bar{\varkappa}\sigma)\right] + \cdots,$$

(2.3-1)

$$h_\lambda(\varkappa\rho) = h_\lambda(\varkappa\sigma) + \left(\frac{\delta}{\sigma}\right) \varkappa\rho_1 h_\lambda'(\varkappa\sigma)$$

$$+ \left(\frac{\delta}{\sigma}\right)^2 \left[\varkappa\rho_2 h_\lambda'(\varkappa\sigma) + \frac{1}{2}\varkappa^2 \rho_1^2 h_\lambda''(\varkappa\sigma)\right] + \cdots,$$

(2.3-2)

and

$$f(\bar{p}\ell p) = f(\bar{p}\ell p)_0 + \left(\frac{\delta}{\sigma}\right) f(\bar{p}\ell p)_1 + \left(\frac{\delta}{\sigma}\right)^2 f(\bar{p}\ell p)_2 + \cdots , \qquad (2.3\text{-}3)$$

we obtain the boundary condition in the following form:

$$\begin{aligned}
0 = \sum_{\ell^a \ell^b \ell \lambda s} \Big\{ & \delta_{p\bar{p}} \Big[j_{\bar{\lambda}}(\bar{\kappa}\sigma) + \left(\frac{\delta}{\sigma}\right) \bar{\kappa}\rho_1 j_{\bar{\lambda}}'(\bar{\kappa}\sigma) \\
& + \left(\frac{\delta}{\sigma}\right)^2 \left(\bar{\kappa}\rho_2 j_{\bar{\lambda}}'(\bar{\kappa}\sigma) + \frac{1}{2}\bar{\kappa}^2 \rho_1^2 j_{\bar{\lambda}}''(\bar{\kappa}\sigma)\right) + \cdots \Big] \\
& + i^{\lambda+1}\lambda \Big[f(\bar{p}\ell p)_0 + \left(\frac{\delta}{\sigma}\right) f(\bar{p}\ell p)_1 + \left(\frac{\delta}{\sigma}\right)^2 f(\bar{p}\ell p)_2 + \cdots \Big] \\
& \times \Big[h_\lambda(\kappa\sigma) + \left(\frac{\delta}{\sigma}\right) \kappa\rho_1 h_\lambda'(\kappa\sigma) + \left(\frac{\delta}{\sigma}\right)^2 \Big(\kappa\rho_2 h_\lambda'(\kappa\sigma) \\
& + \frac{1}{2}\kappa^2 \rho_1^2 h_\lambda''(\kappa\sigma)\Big) + \cdots \Big] \Big\} \, S^{\ell^a \ell^b}_{\ell s \tau - s} \, S^{\ell \lambda}_{\iota \tau 0} \\
& \times D^{\ell^a}(S^a)_{0 s} \, D^{\ell^b}(S^b)_{0 \tau - s} .
\end{aligned}$$

(2.3-4)

We now equate the coefficients of the first three powers of δ/σ to zero and obtain three equations:

<u>Coefficient of the zero power</u>

$$0 = \sum_{\ell^a \ell^b \ell \lambda s} \Big[\delta_{p\bar{p}}\, j_{\bar{\lambda}}(\bar{\varkappa}\sigma)$$

$$+ i^{\lambda+1} \varkappa\, f(\bar{p}\,\ell\, p)_0\, h_\lambda(\varkappa\sigma) \Big]\; S^{\ell^a \ell^b}_{\ell s\, \tau-s}\;\; S^{\ell\lambda}_{i\tau 0}$$

$$\times\, D^{\ell^a}(S^a)_{0s}\, D^{\ell^b}(S^b)_{0\,\tau-s}\,. \qquad (2.3\text{-}5)$$

<u>Coefficient of the first power</u>

$$0 = \sum_{\ell^a \ell^b \ell \lambda s} \Big[\delta_{p\bar{p}}\, \bar{\varkappa}\, \rho_1\, j'_{\bar{\lambda}}(\bar{\varkappa}\sigma)$$

$$i^{\lambda+1} \varkappa\, f(\bar{p}\,\ell\, p)_1\, h_\lambda(\varkappa\sigma) + i^{\lambda+1} \varkappa^2 \rho_1\, f(\bar{p}\,\ell\, p)_0$$

$$\times\, h'_\lambda(\varkappa\sigma) \Big]\;\; S^{\ell^a \ell^b}_{\ell s\, \tau-s}\;\; S^{\ell\lambda}_{i\tau 0}\; D^{\ell^a}(S^a)_{0s}$$

$$\times\, D^{\ell^b}(S^b)_{0\,\tau-s}\,. \qquad (2.3\text{-}6)$$

Coefficient of the second power

$$0 = \sum_{\ell^a \ell^b \ell \lambda s} \Big\{ \delta_{p\bar{p}} \Big[\bar{\kappa}\, \rho_2\, j'_{\bar{\lambda}}(\bar{\kappa}\sigma) + \frac{1}{2} \bar{\kappa}^2 \rho_1^2\, j''_{\bar{\lambda}}(\bar{\kappa}\sigma) \Big] + i^{\lambda+1} \kappa^2 f(\bar{p} \ell p)_0$$

$$\times \Big[\rho_2\, h'_\lambda(\kappa\sigma) + \frac{1}{2} \kappa \rho_1^2\, h''_\lambda(\kappa\sigma) \Big] + i^{\lambda+1} \kappa^2 \rho_1 f(\bar{p} \ell p)_1$$

$$\times h'_\lambda(\kappa\sigma) + i^{\lambda+1} \kappa f(\bar{p} \ell p)_2\, h_\lambda(\kappa\sigma) \Big\}$$

$$\times S^{\ell^a \ell^b}_{\ell s \tau s}\, S^{\ell \lambda}_{\ell \tau 0}\, D^{\ell^a}(S^a)_{0 s}\, D^{\ell^b}(S^b)_{0\, \tau - s}. \tag{2.3-7}$$

The method by which these equations are solved will be illustrated by solving the first, Eq. 2.3-5, in detail. The solution which is thereby obtained, $f(\bar{p} \ell p)_0$, will be inserted into Eq. 2.3-6, which will then be solved for $f(\bar{p} \ell p)_1$. In a similar manner $f(\bar{p} \ell p)_2$ is obtained from Eq. 2.3-7.

Eq. 1.2-10 can be solved for $f(\bar{p} \ell p)$ only for those values of the indices satisfying the conditions

$$|\ell^a - \ell^b| \leq \ell \leq \ell^a + \ell^b, \tag{2.3-8}$$

and

$$|\ell - \lambda| \leq L \leq \ell + \lambda . \tag{2.3-9}$$

This is due to the fact that the product of the Wigner coefficients $S^{\ell^a \ell^b}_{\ell s \tau - s} \; S^{\ell \lambda}_{L \tau 0}$ vanishes unless these conditions are satisfied. It is convenient to introduce a symbol $\Delta(\ell^a \ell^b \ell)$ which is equal to one if Eq. 2.3-8 is satisfied, and equal to zero otherwise. We note that if Eq. 2.3-8 is satisfied then $|\ell - \ell^a| \leq \ell^b \leq \ell + \ell^a$ and $|\ell - \ell^b| \leq \ell^a \leq \ell + \ell^b$. This is clear from the fact that if ℓ^a, ℓ^b, ℓ satisfy Eq. 2.3-8, it is possible to construct a triangle with side lengths ℓ^a, ℓ^b, ℓ. It is also convenient for our purposes to extend the definition of $f(\bar{p} L p)$ by assigning it the value zero when the two "triangle inequalities" are not satisfied.

In order to obtain an explicit expression for $f(\bar{p} L p)$, we first multiply Eq. 2.3-5 by $D^{\ell'^a}(S^a)^*_{0s'} \, D^{\ell'^b}(S^b)_{0\tau-s'}$ and integrate over S^a and S^b. This yields

$$0 = \sum_{\ell\lambda} \Big[\delta_{\ell'^a \bar{\ell}^a}\, \delta_{\ell'^b \bar{\ell}^b}\, \delta_{\ell\bar{\ell}}\, \delta_{\lambda\bar{\lambda}}\, j_{\bar{\lambda}}(\mathcal{H}\sigma)$$

$$+\, i^{\lambda+1}\, \mathcal{H}'\, f(\bar{\ell}^a \bar{\ell}^b \bar{\ell} \bar{\lambda} L \ell'^a \ell'^b \ell \lambda)_0\, h_\lambda(\mathcal{H}'\sigma) \Big]$$

$$\times\, S^{\ell'^a \ell'^b}_{\ell s' \tau - s'}\; S^{\ell\lambda}_{L\tau 0}\,. \qquad (2.3\text{-}10)$$

By the symbol $\mathcal{H}'$ we mean $\mathcal{H}_{\ell'^a \ell'^b}$. We now multiply this equation by $S^{\ell'^a \ell'^b}_{\ell' s' \tau - s'}\, S^{\ell'\lambda'}_{L\tau 0}$ and sum over s' and τ. The unitarity property of the Wigner coefficients states that

$$\sum_{s'} S^{\ell'^a \ell'^b}_{\ell' s' \tau - s'}\; S^{\ell'^a \ell'^b}_{\ell s' \tau - s'} = \delta_{\ell\ell'}\, \Delta(\ell \ell'^a \ell'^b)\,. \qquad (2.3\text{-}11)$$

The presence of $\Delta(\ell \ell'^a \ell'^b)$ on the right hand side of this equation should be emphasized. The Kronecker delta $\delta_{\ell\ell'}$ is equal to one if ℓ equals ℓ'. However, if we do not have $|\ell'^a - \ell'^b| \leq \ell' \leq \ell'^a + \ell'^b$, all the Wigner coefficients in the summation on the left are zero, and the sum is therefore zero. In most listings of identities among Wigner and Racah coefficients, the Δ's are not explicitly written. Omitting them leads to spurious divergences in some of the present applications.

We now have

$$0 = \sum_{\lambda\tau} \Big[\delta_{\ell'^a \bar{\ell}^a}\, \delta_{\ell'^b \bar{\ell}^b}\, \delta_{\ell' \bar{\ell}}\, \delta_{\lambda\bar{\lambda}}\, j_{\bar{\lambda}}(\bar{\kappa}\sigma)$$

$$+\, i^{\lambda+1} \kappa'\, f(\bar{\ell}^a \bar{\ell}^b \bar{\ell} \bar{\lambda} L \ell'^a \ell'^b \ell' \lambda)_0\, h_\lambda(\kappa'\sigma) \Big]$$

$$\times\, \Delta(\ell'^a \ell'^b \ell')\, S^{\ell'\lambda}_{L\tau 0}\, S^{\ell'\lambda'}_{L\tau 0}\,. \qquad (2.3\text{-}12)$$

Carrying out the sums over λ and τ yields finally

$$0 = \Big[\delta_{p\bar{p}}\, j_{\bar{\lambda}}(\bar{\kappa}\sigma) + i^{\lambda+1} \kappa\, f(\bar{p} L p)_0$$

$$\times\, h_\lambda(\kappa\sigma) \Big] \Delta(\ell^a \ell^b \ell)\, \Delta(\ell \lambda L), \qquad (2.3\text{-}13)$$

where we have now dropped the primes from ℓ'^a, ℓ'^b, ℓ', and λ'. As we have previously stated, it is clear that this equation can be solved for $f(\bar{p} L p)_0$ only for values of the indices satisfying Eq. 2.3-8 and Eq. 2.3-9; however, remembering that we have assigned the value zero to $f(\bar{p}Lp)$ if these inequalities are not satisfied, we conclude that

$$f(\bar{p}Lp)_0 = \frac{i^{-\lambda+1}}{\mathcal{H}} \frac{j_\lambda(\mathcal{H}\sigma)}{h_\lambda(\mathcal{H}\sigma)} \delta_{p\bar{p}} \Delta(\ell^a \ell^b \ell) \Delta(\ell \lambda L). \tag{2.3-14}$$

When the result thus obtained for $f(\bar{p}Lp)_0$ is substituted into Eq. 2.3-6 and this equation is solved in an analogous manner we find that

$$f(\bar{p}Lp)_1 = \frac{i^{-\lambda}}{\mathcal{H}\bar{\mathcal{H}}\sigma^2 h_\lambda(\mathcal{H}\sigma) h_{\bar{\lambda}}(\bar{\mathcal{H}}\sigma)} \frac{(2\ell^a+1)(2\ell^b+1)}{(8\pi^2)^2}$$

$$\times \frac{2\lambda+1}{2L+1} \sum_{ss'\tau} S^{\bar{\ell}^a \bar{\ell}^b}_{\bar{\ell}s\tau-s} S^{\ell^a \ell^b}_{\ell s'\tau-s'} S^{\bar{\ell}\bar{\lambda}}_{L\tau 0}$$

$$\times S^{\ell\lambda}_{L\tau c} \int \rho_1(S^a, S^b) D^{\ell^a}(S^a)^*_{0s'}$$

$$\times D^{\bar{\ell}^a}(S^a)_{0s} D^{\ell^b}(S^b)^*_{0\tau-s'} D^{\bar{\ell}^b}(S^b)_{0\tau-s}$$

$$\times dS^a dS^b. \tag{2.3-15}$$

In obtaining this result, we have made use of the fact that[31]

$$j'_{\bar{\lambda}}(\bar{\kappa}\sigma)\,h_{\bar{\lambda}}(\bar{\kappa}\sigma) - j_{\bar{\lambda}}(\bar{\kappa}\sigma)\,h'_{\bar{\lambda}}(\bar{\kappa}\sigma)$$

$$= -\frac{i}{\bar{\kappa}^2\sigma^2}. \qquad (2.3\text{-}16)$$

The result obtained from solving Eq. 2.3-7 is quite lengthy and will be written as the sum of three terms,

$$f(\bar{p}Lp)_2 = A(\bar{p}Lp) + B(\bar{p}Lp) + C(\bar{p}Lp), \qquad (2.3\text{-}17)$$

where

$$A(\bar{p}Lp) = \frac{i^{-\lambda}}{\bar{\kappa}\kappa\sigma^2 h_{\lambda}(\kappa\sigma)\,h_{\bar{\lambda}}(\bar{\kappa}\sigma)}\;\frac{(2l^a+1)(2l^b+1)}{(8\pi^2)^2}$$

$$\times \frac{2\lambda+1}{2L+1} \sum_{ss'\tau} S^{l^a l^b}_{l s' \tau-s'}\, S^{\bar{l}^a \bar{l}^b}_{\bar{l} s \tau-s}\, S^{l\lambda}_{L\tau 0}\, S^{\bar{l}\bar{\lambda}}_{L\tau 0}$$

$$\times \int \rho_2(S^a, S^b)\, D^{l^a}(S^a)^{*}_{0s'}\, D^{\bar{l}^a}(S^a)_{0s}\, D^{l^b}(S^b)^{*}_{0\tau-s'}$$

$$\times D^{\bar{l}^b}(S^b)_{0\tau-s}\, dS^a dS^b, \qquad (2.3\text{-}18)$$

$$B(\bar{p}\,L\,p) = \frac{\bar{\mathcal{H}}^2}{2\mathcal{H}} \frac{i^{-\lambda+1}}{h_\lambda(\mathcal{H}\sigma)\,h_{\bar{\lambda}}(\bar{\mathcal{H}}\sigma)} \frac{(2\ell^a+1)(2\ell^b+1)}{(8\pi^2)^2}$$

$$\times \frac{2\lambda+1}{2L+1}\Big[\,j_{\bar{\lambda}}''(\bar{\mathcal{H}}\sigma)\,h_{\bar{\lambda}}(\bar{\mathcal{H}}\sigma)$$

$$-\,j_{\bar{\lambda}}(\bar{\mathcal{H}}\sigma)\,h_{\bar{\lambda}}''(\bar{\mathcal{H}}\sigma)\Big] \sum_{s s' \tau} S^{\ell^a \ell^b}_{\ell s' \tau - s'}$$

$$\times S^{\bar{\ell}^a \bar{\ell}^b}_{\bar{\ell} s \tau - s}\; S^{\ell \lambda}_{L \tau 0}\; S^{\bar{\ell}\bar{\lambda}}_{L \tau 0}$$

$$\times \int \left[\rho_1(S^a, S^b)\right]^2 D^{\ell^a}(S^a)^*_{0 s'}\, D^{\bar{\ell}^a}(S^a)_{0 s}$$

$$\times D^{\ell^b}(S^b)^*_{0\, \tau - s'}\, D^{\bar{\ell}^b}(S^b)_{0\, \tau - s}\, dS^a\, dS^b\,,$$

(2.3-19)

and

$$C(\bar{p}Lp) = \frac{i^{-\lambda+1}}{\mathcal{H}\, h_\lambda(\mathcal{H}\sigma)} \; \frac{(2\ell^a+1)(2\ell^b+1)}{(8\pi^2)^2}$$

$$\times \frac{2\lambda+1}{2L+1} \sum_{\substack{\tilde{\ell}^a \tilde{\ell}^b \tilde{\ell} \\ \tilde{\lambda}\, s s' \tau}} i^{\tilde{\lambda}+1}\, \tilde{\mathcal{H}}^2 f(\bar{p}L\tilde{p})_1\, h'_{\tilde{\lambda}}(\tilde{\mathcal{H}}\sigma)$$

$$\times S^{\tilde{\ell}^a \tilde{\ell}^b}_{\tilde{\ell} s \tau - s}\, S^{\ell^a \ell^b}_{\ell s' \tau - s'}\, S^{\tilde{\ell}\tilde{\lambda}}_{L \tau 0}\, S^{\ell \lambda}_{L \tau 0} \int \rho_1(S^a; S^b)$$

$$\times D^{\ell^a}(S^a)^*_{0s'}\, D^{\tilde{\ell}^a}(S^a)_{0s}\, D^{\ell^b}(S^b)^*_{0\tau-s'}$$

$$\times D^{\tilde{\ell}^b}(S^b)_{0\tau-s}\, dS^a dS^b. \qquad (2.3\text{-}20)$$

In the expression for C, $\tilde{\ell}^a \tilde{\ell}^b \tilde{\ell}\, \tilde{\lambda}$ are four ℓ-type summation indices. The symbol $\tilde{\mathcal{H}}$ stands for $\mathcal{H}_{\tilde{\ell}^a \tilde{\ell}^b}$.

In these three rather formidable looking expressions we have the means for computing $f(\bar{p}Lp)_2$. The general procedure to be followed will be to insert the explicit expressions for $\rho_1(S^a; S^b)$ and $\rho_2(S^a; S^b)$ into these expressions, carry out the integrations over the angles by use of the formulas given in Appendix I, and to use various orthogonality relationships among the Wigner and the Racah coefficients in order to reduce the multiple sums which occur to sums over a single index.

Section 2.4 The Evaluation of $f(\bar{p}Lp)_1$

When Eq. 2.2-11, which gives the expression for $\rho_1(S^a, S^b)$, is substituted into Eq. 2.3-15, the following expression is obtained:

$$f(\bar{p}Lp)_1 = \frac{i^{-\lambda}}{\varkappa\bar{\varkappa}\sigma h_\lambda(\varkappa\sigma) h_{\bar{\lambda}}(\bar{\varkappa}\sigma)} \frac{(2\ell^a+1)(2\ell^b+1)}{(8\pi^2)^2}$$

$$\times \frac{2\lambda+1}{2L+1} \sum_{ss'\tau} S^{\ell^a\ell^b}_{\ell s'\tau-s'} S^{\bar{\ell}^a\bar{\ell}^b}_{\bar{\ell}s\tau-s} S^{\ell\lambda}_{L\tau 0} S^{\bar{\ell}\bar{\lambda}}_{L\tau 0}$$

$$\times \int \left[D^1(S^b)_{00} - D^1(S^a)_{00} \right] D^{\ell^a}(S^a)^*_{0s'} D^{\bar{\ell}^a}(S^a)_{0s}$$

$$\times D^{\ell^b}(S^b)^*_{0\tau-s'} D^{\bar{\ell}^b}(S^b)_{0\tau-s} \, dS^a dS^b . \tag{2.4-1}$$

Upon carrying out the angle integrations we find that

$$\int \left[D'(S^b)_{00} - D'(S^a)_{00} \right] D^{l^a}(S^a)^*_{0s'}\, D^{\bar{l}^a}(S^a)_{0s}$$

$$\times D^{l^b}(S^b)^*_{0\tau-s'}\, D^{\bar{l}^b}(S^b)_{0\tau-s}\, dS^a dS^b = \frac{(8\pi^2)^2}{(2l^a+1)(2l^b+1)}$$

$$\times \left[\delta_{l^a\bar{l}^a} S^{1\bar{l}^b}_{l^b00}\, S^{1\bar{l}^b}_{l^b0\tau-s} - \delta_{l^b\bar{l}^b} S^{1\bar{l}^a}_{l^a00}\, S^{1\bar{l}^a}_{l^a0s} \right] \delta_{ss'}$$

(2.4-2)

Hence

$$f(\bar{p}Lp)_1 = \frac{i^{-\lambda}}{\mathcal{H}\bar{\mathcal{H}}\,\sigma\, h_\lambda(\mathcal{H}\sigma)\, h_{\bar{\lambda}}(\bar{\mathcal{H}}\sigma)} \quad \frac{2\lambda+1}{2L+1}$$

$$\times \sum_{s\tau} \left[S^{l^a\bar{l}^b}_{\bar{l}s\tau-s}\, S^{l^al^b}_{ls\tau-s}\, S^{\bar{l}\bar{\lambda}}_{L\tau0}\, S^{l\lambda}_{L\tau0} \right.$$

$$\times S^{1\bar{l}^b}_{l^b00}\, S^{1\bar{l}^b}_{l^b0\tau-s}\, \delta_{l^a\bar{l}^a} - S^{\bar{l}^al^b}_{\bar{l}s\tau-s}\, S^{l^al^b}_{ls\tau-s}$$

$$\left. \times S^{\bar{l}\bar{\lambda}}_{L\tau0}\, S^{l\lambda}_{L\tau0}\, S^{1\bar{l}^a}_{l^a00}\, S^{1\bar{l}^a}_{l^a0s}\, \delta_{l^b\bar{l}^b} \right].$$

(2.4-3)

Finally, by making use of Eqs. A.2-1 and A.2-2 (an equation number such as A.2-1 refers to Eq. 1 of Appendix II), we may write this result in terms of Racah coefficients. Thus

$$f(\bar{p}Lp)_1 = \frac{i^{-\lambda}}{\mathcal{H}\bar{\mathcal{H}}\sigma\, h_\lambda(\mathcal{H}\sigma)\, h_{\bar{\lambda}}(\bar{\mathcal{H}}\sigma)} \; (2\lambda+1)$$

$$\times \sqrt{\frac{(2\ell+1)(2\bar{\ell}+1)}{2\bar{\lambda}+1}} \; S^{1\lambda}_{\bar{\lambda}00} \, W(\bar{\ell}\, 1\, L\, \lambda\, \ell\, \bar{\lambda})$$

$$\times \Big[(-1)^{\ell^b+\bar{\ell}^b+1} \sqrt{2\ell^b+1} \; S^{1\bar{\ell}^b}_{\ell^b 00} \, \delta_{\ell^a \bar{\ell}^a} \, W(1\,\bar{\ell}^b\,\ell\,\ell^a\,\ell^b\,\bar{\ell})$$

$$- (-1)^{\ell+\bar{\ell}+1} \sqrt{2\ell^a+1} \; S^{1\bar{\ell}^a}_{\ell^a 00} \, \delta_{\ell^b \bar{\ell}^b} \, W(1\,\bar{\ell}^a\,\ell\,\ell^b\,\ell^a\,\bar{\ell}) \Big] .$$

(2.4-4)

Section 2.5 <u>The Evaluation of $f(\bar{p}Lp)_2$</u>

The expression for $f(\bar{p}Lp)_2$ is obtained in much the same manner as were $f(\bar{p}Lp)_0$ and $f(\bar{p}Lp)_1$. The expression

$$\rho_2(S^a, S^b) = \sigma \Big[\underset{(1)}{-\tfrac{2}{3}} + \underset{(2)}{\tfrac{1}{3} D^2(S^a)_{00}}$$

$$\underset{(3)}{- D^1(S^a)_{0-1} D^1(S^b)_{01}} \; \underset{(4)}{- D^1(S^a)_{01} D^1(S^b)_{0-1}} \; \underset{(5)}{+ \tfrac{1}{3} D^2(S^b)_{00}} \Big]$$

(2.5-1)

must be introduced into the expression for A, Eq. 2.3-18. This will be done one term at a time, and the number in parentheses under the term will be added to A as a subscript. It will turn out that in order to evaluate the cross section we shall need only those elements of $f(\bar{p}\,L\,p)_\Omega$ for which p is equal to $\bar{p}$. We therefore compute only those elements. Thus

$$A_1(p\,L\,p) = - \frac{2\, i^{-\lambda}}{3 \mathcal{H}^2 \sigma\, k_\lambda^2(\mathcal{H}\sigma)} \frac{(2\ell^a+1)(2\ell^b+1)}{(8\pi^2)^2}$$

$$\times \frac{2\lambda+1}{2L+1} \sum_{s s' \tau} S^{\ell^a \ell^b}_{\ell s \tau - s} \, S^{\ell^a \ell^b}_{\ell s' \tau - s'} \left(S^{\ell \lambda}_{L \tau 0} \right)^2$$

$$\times \int D^{\ell^a}(S^a)^*_{0 s'} \, D^{\ell^a}(S^a)_{0 s} \, D^{\ell^b}(S^b)^*_{0 \tau - s'}$$

$$\times D^{\ell^b}(S^b)_{0 \tau - s} \, dS^a \, dS^b .$$

(2.5-2)

Making use of the orthogonality of the D 's, Eq. A.1-2, we carry out the integration over S^a and S^b to obtain

$$A_1(pLp) = -\frac{2i^{-\lambda}}{3\mathcal{H}^2\sigma\, h_\lambda^2(\mathcal{H}\sigma)} \frac{2\lambda+1}{2L+1}$$

$$\times \sum_{s\tau} (S^{\ell^a\ell^b}_{\ell s \tau-s})^2 (S^{\ell\lambda}_{L\tau 0})^2 = -\frac{2i^{-\lambda}}{3\mathcal{H}^2\sigma}$$

$$\times \frac{1}{h_\lambda^2(\mathcal{H}\sigma)} \Delta(\ell^a\ell^b\ell)\,\Delta(L\lambda\ell). \qquad (2.5\text{-}3)$$

This completes the evaluation of A_1.

The expression for A_2 is

$$A_2(pLp) = \frac{i^{-\lambda}}{3\mathcal{H}^2\sigma\, h_\lambda^2(\mathcal{H}\sigma)} \frac{(2\ell^a+1)(2\ell^b+1)}{(8\pi^2)^2}$$

$$\times \frac{2\lambda+1}{2L+1} \sum_{ss'\tau} S^{\ell^a\ell^b}_{\ell s\tau-s} S^{\ell^a\ell^b}_{\ell s'\tau-s'} (S^{\ell\lambda}_{L\tau 0})^2$$

$$\times \int D^2(S^a)_{00} D^{\ell^a}(S^a)^*_{0s'} D^{\ell^a}(S^a)_{0s} D^{\ell^b}(S^b)^*_{0\tau-s'}$$

$$\times D^{\ell^b}(S^b)_{0\tau-s}\, dS^a dS^b = \frac{i^{-\lambda}}{3\mathcal{H}^2\sigma\, h_\lambda^2(\mathcal{H}\sigma)}$$

$$\times \frac{2\lambda+1}{2L+1} \sum_{s\tau} (S^{\ell^a\ell^b}_{\ell s\tau-s})^2 (S^{\ell\lambda}_{L\tau 0})^2 S^{2\ell^a}_{\ell^a 00} S^{2\ell^a}_{\ell^a 0 s}. \qquad (2.5\text{-}4)$$

Making use of Eqs. A.2-1 and A.2-2, we are again able to write the result in terms of Racah coefficients. . Thus we find that

$$A_2(p L p) = \frac{i^{-\lambda}}{3\varkappa^2 \sigma\, h_\lambda^2(\varkappa\sigma)} (2\ell+1)\sqrt{(2\ell^a+1)(2\lambda+1)}$$

$$\times S^{2\ell^a}_{\ell^a 00}\, S^{2\lambda}_{\lambda 00}\, W(2\ell^a \ell \ell^b \ell^a \ell)\, W(\ell 2 L \lambda \ell \lambda).$$

(2.5-5)

The quantity $A_3(p L p)$ is obtained by inserting the product $D^1(S^a)_{0-1}\, D^1(S^b)_{01}$ into the expression for $A(p L p)$. We obtain

$$A_3(p L p) = -\frac{i^{-\lambda}}{\varkappa^2 \sigma\, h_\lambda(\varkappa\sigma)} \cdot \frac{(2\ell^a+1)(2\ell^b+1)}{(8\pi^2)^2}$$

$$\times \frac{2\lambda+1}{2L+1} \sum_{s s' \tau} S^{\ell^a \ell^b}_{\ell s \tau - s}\, S^{\ell^a \ell^b}_{\ell s' \tau - s'}\, (S^{\ell\lambda}_{L \tau 0})^2$$

$$\times \int D^1(S^a)_{0-1}\, D^{\ell^a}(S^a)^*_{0s'}\, D^{\ell^a}(S^a)_{0s}\, D^1(S^b)_{01}$$

$$\times D^{\ell^b}(S^b)^*_{0\tau-s'}\, D^{\ell^b}(S^b)_{0\tau-s}\, dS^a\, dS^b. \quad (2.5\text{-}6)$$

From Eq. A.1-4 we find that

$$\int D^{1}(S^{a})_{0-1} D^{\ell^{a}}(S^{a})^{*}_{0s'} D^{\ell^{a}}(S^{a})_{0s}\, dS^{a}$$

$$= \frac{8\pi^{2}}{2\ell^{a}+1} S^{1\ell^{a}}_{\ell^{a}00} S^{1\ell^{a}}_{\ell^{a},-1,s} \delta_{s',s-1} . \qquad (2.5\text{-}7)$$

However, any Wigner coefficient $S^{\ell_1\ell_2}_{\ell_3 00}$ is zero if the sum $\ell_1+\ell_2+\ell_3$ is an odd integer. Thus

$$A_3(p\,L\,p) = 0. \qquad (2.5\text{-}8)$$

In an analogous manner we find that

$$A_4(p\,L\,p) = 0. \qquad (2.5\text{-}9)$$

Finally, we need $A_5(pLp)$. However, this is easily shown to be the same as $A_2(pLp)$ with the ℓ^{a} and ℓ^{b} interchanged. Hence

$$A_5(pLp) = \frac{i^{-\lambda}}{3\mathcal{H}^{2}\sigma\, k_{\lambda}^{2}(\mathcal{H}\sigma)} (2\ell+1)\sqrt{(2\ell^{b}+1)(2\lambda+1)}$$

$$\times S^{2\ell^{b}}_{\ell\ell^{b}00} S^{2\lambda}_{\lambda 00} W(2\ell^{b}\ell\ell^{a}\ell^{b}\ell)W(\ell 2 L\lambda\ell\lambda).$$

(2.5-10)

The expression for $B(p L p)$ is given by Eq. 2.3-19. The combination of spherical Bessel functions appearing in this equation is just the derivative with respect to $\bar{\mathcal{H}}\sigma$ of the left side of Eq. 2.3-16. Thus

$$j_{\bar{\lambda}}''(\bar{\mathcal{H}}\sigma)h_{\bar{\lambda}}(\bar{\mathcal{H}}\sigma) - j_{\bar{\lambda}}(\bar{\mathcal{H}}\sigma)h_{\bar{\lambda}}''(\bar{\mathcal{H}}\sigma) = \frac{2i}{\bar{\mathcal{H}}^3\sigma^3}. \tag{2.5-11}$$

As in the evaluation of $A(pLp)$ we write

$$\rho_1^2(S^a, S^b) = \underset{(1)}{\sigma^2[D'(S^a)_{00}]^2} - \underset{(2)}{2\sigma^2 D'(S^a)_{00} D'(S^b)_{00}} + \underset{(3)}{\sigma^2[D'(S^b)_{00}]^2}, \tag{2.5-12}$$

where again the numbers in parentheses below the individual terms are added to B as a subscript. Then, from Eq. 2.3-19 we have

$$B_1(pLp) = -\frac{i^{-\lambda}}{\mathcal{H}^2\sigma h_\lambda^2(\mathcal{H}\sigma)} \frac{(2\ell^a+1)(2\ell^b+1)}{(8\pi^2)^2}$$

$$\times \frac{2\lambda+1}{2L+1} \sum_{ss'\tau} S^{\ell^a\ell^b}_{\ell s\tau-s} S^{\ell^a\ell^b}_{\ell s'\tau-s'} (S^{\ell\lambda}_{L\tau 0})^2$$

$$\times \int [D'(S^a)_{00}]^2 D^{\ell^a}(S^a)^*_{0s'} D^{\ell^a}(S^a)_{0s} D^{\ell^b}(S^b)^*_{0\tau-s'}$$

$$\times D^{\ell^b}(S^b)_{0\tau-s}\, dS^a dS^b. \tag{2.5-13}$$

Now by Eq. A.1-3, we have

$$\left[D^{1}(S^{a})_{00}\right]^{2} = \sum_{q} (S^{11}_{q00})^{2} D^{q}(S^{a})_{00}. \tag{2.5-14}$$

Hence the integral over S^{a} becomes

$$\sum_{q} (S^{11}_{q00})^{2} \int D^{q}(S^{a})_{00}\, D^{\ell^{a}}(S^{a})^{*}_{0s'}$$

$$\times D^{\ell^{a}}(S^{a})_{0s}\, dS^{a} = \frac{8\pi^{2}}{2\ell^{a}+1} \sum_{q} (S^{11}_{q00})^{2}$$

$$\times S^{q\ell^{a}}_{\ell^{a}00}\, S^{q\ell^{a}}_{\ell^{a}0s}\, \delta_{ss'}. \tag{2.5-15}$$

So

$$B_{1}(p\,\iota\,p) = -\frac{i^{-\lambda}}{\mathcal{H}^{2}\sigma\, h_{\lambda}^{2}(\mathcal{H}\sigma)}\ \frac{2\lambda+1}{2L+1}$$

$$\times \sum_{sqr} (S^{\ell^{a}\ell^{b}}_{\ell s r-s})^{2} (S^{\ell\lambda}_{Lr0})^{2} (S^{11}_{q00})^{2}\ S^{q\ell^{a}}_{\ell^{a}00}$$

$$\times S^{q\ell^{a}}_{\ell^{a}0s}. \tag{2.5-16}$$

Using Eq. A.2-1 this can be written

$$B_1(plp) = -\frac{i^{-\lambda}}{\varkappa^2 \sigma h_\lambda^2(\varkappa\sigma)} (2l+1)$$

$$\times\sqrt{(2l^a+1)(2\lambda+1)} \sum_q (-1)^q (S''_{q00})^2 S^{q l^a}_{l^a 00}$$

$$\times S^{q\lambda}_{\lambda 00} W(q l^a l l^b l^a l) W(l q l \lambda l \lambda). \tag{2.5-17}$$

In $B_2(plp)$ there appears the integral

$$\int D^{l^a}(S^a)^*_{0s'} D^{l^a}(S^a)_{0s} D^1(S^a)_{00}\, dS^a$$

$$= \frac{8\pi^2}{2l^a+1} S^{1l^a}_{l^a 00} S^{1l^a}_{l^a 0s} \delta_{ss'}. \tag{2.5-18}$$

But $S^{1l^a}_{l^a 00}$ is equal to zero, since the sum of the three indices, $2l^a+1$, is an odd integer. So we find that

$$B_2(plp) = 0. \tag{2.5-19}$$

The quantity $\mathcal{B}_3(pLp)$ is $\mathcal{B}_1(pLp)$ with ℓ^a and ℓ^b interchanged. Hence

$$\mathcal{B}_3(pLp) = -\frac{i^{-\lambda}}{\mathcal{H}^2\sigma\, h_\lambda^2(\mathcal{H}\sigma)}(2\ell+1)\sqrt{(2\lambda+1)(2\ell^b+1)}$$

$$\times\sum_{g}(-1)^g\left(S_{g00}^{11}\right)^2 S_{\ell^b00}^{g\ell^b} S_{\lambda00}^{g\lambda} W(g\ell^b\ell\ell^a\ell^b\ell)$$

$$\times W(\ell g L\lambda\ell\lambda). \qquad (2.5\text{-}20)$$

In order to complete the evaluation of $f(pLp)_2$ we must now compute $C(pLp)$ which is given by Eq. 2.3-20. This is the most difficult of the terms to evaluate since it contains both $f(\bar{p}Lp)_1$, given by Eq. 2.4-4 and $\rho_1(S^a, S^b)$, given by Eq. 2.2-11. When these substitutions are made we find that

$$C(pLp) = -\frac{i^{-\lambda}}{\mathcal{H}^2 h_\lambda^2(\mathcal{H}\sigma)}\frac{\sqrt{(2\ell+1)(2\lambda+1)}}{2L+1}$$

$$\sum_{\substack{\tilde{\ell}^a\tilde{\ell}^b\tilde{\ell} \\ \tilde{\lambda}s\tau}}\left\{\tilde{\mathcal{H}}\frac{h_{\tilde{\lambda}}'(\tilde{\mathcal{H}}\sigma)}{h_{\tilde{\lambda}}(\tilde{\mathcal{H}}\sigma)}(2\tilde{\lambda}+1)\sqrt{2\tilde{\ell}+1}\, W(\ell 1 L\tilde{\lambda}\tilde{\ell}\lambda)\right.$$

$$\times S_{\lambda00}^{1\tilde{\lambda}}\left[(-1)^{\tilde{\ell}^b+\ell^b+1}\sqrt{2\tilde{\ell}^b+1}\; S_{\tilde{\ell}^b00}^{1\ell^b}\;\delta_{\tilde{\ell}^a\ell^a}\right.$$

$$\times W(1\ell^b\tilde{\ell}\tilde{\ell}^a\tilde{\ell}^b\ell) - (-1)^{\tilde{\ell}+\ell+1}\cdot\sqrt{2\tilde{\ell}^a+1}\; S_{\tilde{\ell}^a00}^{1\ell^a}$$

$$\times\, \delta_{\tilde{l}^b \tilde{l}^b}\, W(1\, l^a\, \tilde{l}\, \tilde{l}^b\, \tilde{l}^a\, l)\Big]\Big[S^{l^a \tilde{l}^b}_{\tilde{l}^s\, r-s}\, S^{l^a l^b}_{l^s\, r-s}\, S^{\tilde{l}\tilde{\lambda}}_{l\, r\, 0}$$

$$\times\, S^{l\lambda}_{l\, r\, 0}\, S^{1\tilde{l}^b}_{l^b\, 0\, 0}\, S^{1\tilde{l}^b}_{l^b\, 0\, r-s}\, \delta_{l^a \tilde{l}^a} - S^{\tilde{l}^a l^b}_{\tilde{l}^s\, r-s}\, S^{l^a l^b}_{l^s\, r-s}$$

$$\times\, S^{\tilde{l}\tilde{\lambda}}_{l\, r\, 0}\, S^{l\lambda}_{l\, r\, 0}\, S^{1\tilde{l}^a}_{l^a\, 0\, 0}\, S^{1\tilde{l}^a}_{l^a\, 0\, s}\, \delta_{l^b \tilde{l}^b}\Big]\Big\}. \qquad (2.5\text{-}21)$$

Consider now the product of the two expressions in brackets in Eq. 2.5-21. When the first term of the first bracket multiplies the second term of the second bracket there will occur the product $S^{1 l^b}_{\tilde{l}^b\, 0\, 0}\, \delta_{l^b \tilde{l}^b}$ which, as has been previously mentioned, is equal to zero. In like manner, the product of the second term of the first bracket with the first term of the second bracket is zero. We then make use once again of Eqs. A.2-1 and A.2-2 to obtain

$$
\begin{aligned}
C(pLp) = &- \frac{i^{-\lambda}}{\kappa^2 h_\lambda^2(\kappa\sigma)} (2\lambda+1)(2\ell+1) \\
&\sum_{\ell^a \tilde{\ell}^a \ell^b \tilde{\ell} \tilde{\lambda}} \Bigg\{ \tilde{\kappa} \frac{h'_{\tilde{\lambda}}(\tilde{\kappa}\sigma)}{h_{\tilde{\lambda}}(\tilde{\kappa}\sigma)} (2\tilde{\ell}+1) (S^{1\lambda}_{\tilde{\lambda}00})^2 \\
&\times W^2(\ell 1 L \tilde{\lambda} \tilde{\ell} \lambda) \Big[(2\ell^a+1) (S^{1\ell^a}_{\tilde{\ell}^a 00})^2 \delta_{\ell^b \tilde{\ell}^b} \\
&\times W^2(1 \ell^a \tilde{\ell} \ell^b \tilde{\ell}^a \ell) + (2\ell^b+1) (S^{1\ell^b}_{\tilde{\ell}^b 00})^2 \delta_{\ell^a \tilde{\ell}^a} \\
&\times W^2(1 \ell^b \tilde{\ell} \ell^a \tilde{\ell}^b \ell) \Big] \Bigg\} . \qquad (2.5\text{-}22)
\end{aligned}
$$

This completes the evaluation of the first three terms in the expansion of the scattering amplitude in powers of δ/σ .

CHAPTER III

THE CROSS SECTION

In this chapter we calculate the cross section for the scattering of two loaded spheres in the form of a power series in δ/σ . This is accomplished by using the expression obtained by Gioumousis and Curtiss for the cross section in terms of the scattering amplitude, an explicit expression for which was obtained in Chapter II.

Section 3.1 The Expansion of the Cross Section in Powers of δ/σ

In Chapter I the cross section for the collision of two rigid bodies was given. For this quantity we used the symbol

$$I(T|\bar{\ell}^a \bar{m}^a \bar{\ell}^b \bar{m}^b, \ell^a m^a \ell^b m^b|R), \qquad (3.1\text{-}1)$$

where T specifies the direction of motion of the incident molecule, and R the direction of motion of the scattered molecule. As was mentioned in Chapter I, however, McCourt and Snider have shown that a knowledge of the so-called degeneracy averaged cross section is normally sufficient for the evaluation of the transport coefficients. This is defined as the result of averaging the cross section in Eq. 3.1-1 over the initial m values $\bar{m}^a$ and $\bar{m}^b$, and summing it over the final values, m^a and m^b. Since there are $2\ell+1$ values of m

for each value of $\mathcal{l}$ we are led to the following definition of the degeneracy averaged cross section:

$$I(T|\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|R) = \frac{1}{(2\bar{\ell}^a+1)(2\bar{\ell}^b+1)}$$

$$\times \sum_{\substack{\bar{m}^a\bar{m}^b \\ m^a m^b}} I(T|\bar{\ell}^a\bar{m}^a\bar{\ell}^b\bar{m}^b, \ell^a m^a \ell^b m^b|R). \tag{3.1-2}$$

It is shown by Gioumousis and Curtiss that this averaged cross section, which will henceforth be referred to simply as the cross section, may be written in the form

$$I(T|\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|R) = \sum_{J=0}^{\infty} I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)$$

$$\times D^J(RT^{-1})_{00}. \tag{3.1-3}$$

From the expression for the representation coefficients, Eq. 2.2-8, it can be seen that a coefficient of the form $D^J(RT^{-1})_{00}$ is a function only of the second Eulerian angle of RT^{-1}. This angle is the angle χ between the directions of T and R.

Thus we arrive at the conclusion that the degeneracy averaged cross section does not depend individually upon the directions of T and R, but only upon their relative direction.

From Eq. 3.1-3 we see that a knowledge of the expansion coefficients $I(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | J)$ is tantamount to a knowledge of the cross section itself. However, as is true in the classical theory of transport phenomena, it is not the cross section itself which is required, but only certain moments of the cross section. In order to calculate the transport coefficients in the quantum case we shall require $I(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | J)$ only for J equal to 0, 1, and 2. We now proceed with the explicit evaluation of these quantities for the loaded sphere model.

The formula for the expansion coefficients in Eq. 3.1-3 is[27]

$$I(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | J) = \frac{1}{(2\ell^a+1)(2\ell^b+1)} \frac{\mathcal{H}}{\mathcal{H}}$$

$$\times \sum_{\substack{\bar{\ell} \bar{\lambda} \ell \lambda \\ \bar{\lambda}' \lambda' L L'}} i^{\bar{\lambda}-\bar{\lambda}'} (-1)^{\ell+\bar{\ell}} (2L+1)(2L'+1)(2\bar{\lambda}+1)(2\bar{\lambda}'+1)$$

$$\times S_{J00}^{\bar{\lambda}\bar{\lambda}'} S_{J00}^{\lambda\lambda'} W(L\lambda L'\lambda'\ell J) W(L\bar{\lambda} L'\bar{\lambda}'\bar{\ell} J)$$

$$\times f(\bar{\ell}^a \bar{\ell}^b \bar{\ell} \bar{\lambda} L \ell^a \ell^b \ell \lambda) f(\bar{\ell}^a \bar{\ell}^b \bar{\ell} \bar{\lambda}' L' \ell^a \ell^b \ell \lambda')^* . \tag{3.1-4}$$

The quantity $f(\bar{p}Lp)$ which appears in this equation is the scattering amplitude which we have evaluated explicitly in Chapter II. When the expansion of $f(\bar{p}Lp)$ in powers of δ/σ, Eq. 2.3-3, is inserted into Eq. 3.1-4 an expansion of $I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)$ in powers of δ/σ is obtained. Using a notation analogous to that used in the expansion of $f(\bar{p}Lp)$ we write

$$I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J) = I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_0$$

$$+\left(\frac{\delta}{\sigma}\right)I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_1 + \left(\frac{\delta}{\sigma}\right)^2 I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 + \cdots.$$

(3.1-5)

In order to evaluate the coefficients of the successive powers of δ/σ in this expansion we must first write the product of f 's which appears in Eq. 3.1-4 in a series:

$$f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}L\ell^a\ell^b\ell\lambda)\,f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}'L'\ell^a\ell^b\ell\lambda')^*$$

$$= f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}L\ell^a\ell^b\ell\lambda)_0\,f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}'L'\ell^a\ell^b\ell\lambda')_0^*$$

$$+\left(\frac{\delta}{\sigma}\right)\Big[f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}L\ell^a\ell^b\ell\lambda)_0\,f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}'L'\ell^a\ell^b\ell\lambda')_1^*$$

$$+ f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}L\ell^a\ell^b\ell\lambda)_1\, f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}'L'\ell^a\ell^b\ell\lambda')_0^*\Big]$$

$$+\left(\frac{\delta}{\sigma}\right)^2\Big[f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}L\ell^a\ell^b\ell\lambda)_0\, f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}'L'\ell^a\ell^b\ell\lambda')_2^*$$

$$+ f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}L\ell^a\ell^b\ell\lambda)_1\, f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}'L'\ell^a\ell^b\ell\lambda')_1^*$$

$$+ f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}L\ell^a\ell^b\ell\lambda)_2\, f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}'L'\ell^a\ell^b\ell\lambda')_0^*\Big]. \tag{3.1-6}$$

We now insert this expression into Eq. 3.1-4 to obtain $I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_j$ for j equal to 0, 1, and 2 .

Section 3.2 The Evaluation of $I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_0$ and $I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_1$

An equation for $I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_0$ is obtained when the first term in Eq. 3.1-6 is inserted into Eq. 3.1-4. The explicit expression for $f(\bar{p}Lp)_0$ is given by Eq. 2.3-14. After carrying out the indicated summations over $\bar{\ell}$, $\bar{\lambda}$, and $\bar{\lambda}'$, we obtain

$$I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_0 = \frac{1}{(2\ell^a+1)(2\ell^b+1)}\,\delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}$$

$$\times\frac{1}{\mathcal{H}^2}\sum_{\ell\lambda\lambda' L L'}(2L+1)(2L'+1)(2\lambda+1)(2\lambda'+1)$$

$$\times\left(S^{\lambda\lambda'}_{J00}\right)^2 W^2(L\lambda L'\lambda'\ell J)$$

$$\times\frac{j_\lambda(\mathcal{H}\sigma)\,j_{\lambda'}(\mathcal{H}\sigma)}{h_\lambda(\mathcal{H}\sigma)\,h^*_{\lambda'}(\mathcal{H}\sigma)}\,\Delta(\ell\ell^a\ell^b). \tag{3.2-1}$$

The sum over L' may be carried out by the use of Eq. A.1-12. This yields

$$I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_0 = \frac{1}{(2\ell^a+1)(2\ell^b+1)}\,\delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}$$

$$\times\frac{1}{\mathcal{H}^2}\sum_{\ell\lambda\lambda' L}(2L+1)(2\lambda'+1)\left(S^{\lambda\lambda'}_{J00}\right)^2\frac{j_\lambda(\mathcal{H}\sigma)\,j_{\lambda'}(\mathcal{H}\sigma)}{h_\lambda(\mathcal{H}\sigma)\,h^*_{\lambda'}(\mathcal{H}\sigma)}$$

$$\times\Delta(L\lambda\ell)\,\Delta(\ell^a\ell^b\ell). \tag{3.2-2}$$

We must now evaluate the sum

$$\sum_{\ell L}(2L+1)\,\Delta(L\lambda\ell)\,\Delta(\ell^a\ell^b\ell). \tag{3.2-3}$$

Making use of the formula

$$\sum_{j=0}^{n}(2j+1) = (n+1)^2, \tag{3.2-4}$$

we obtain

$$\sum_{L}(2L+1)\Delta(L\lambda\ell) = \sum_{L=|\lambda-\ell|}^{\lambda+\ell}(2L+1) = \sum_{L=0}^{\lambda+\ell}(2L+1)$$

$$-\sum_{L=0}^{|\lambda-\ell|-1}(2L+1) = (\lambda+\ell+1)^2 - |\lambda-\ell|^2 = (2\ell+1)(2\lambda+1). \tag{3.2-5}$$

Hence

$$\sum_{\ell L}(2L+1)\Delta(L\lambda\ell)\Delta(\ell^a_\ell{}^b_\ell) = (2\lambda+1)\sum_{\ell}(2\ell+1)\Delta(\ell^a_\ell{}^b_\ell)$$

$$= (2\lambda+1)(2\ell^a+1)(2\ell^b+1). \tag{3.2-6}$$

Using this result in Eq. 3.2-2 gives

$$I(\bar{\ell}^a_{\bar{\ell}}{}^b\ell^a_\ell{}^b|J)_0 = \delta_{\ell^a_{\bar{\ell}}{}^a}\,\delta_{\ell^b_{\bar{\ell}}{}^b}\,\frac{1}{\mathcal{H}^2}\sum_{\lambda\lambda'}(2\lambda+1)$$

$$\times(2\lambda'+1)\left(S_{500}^{\lambda\lambda'}\right)^2\frac{j_\lambda(\mathcal{H}\sigma)j_{\lambda'}(\mathcal{H}\sigma)}{h_\lambda(\mathcal{H}\sigma)h^*_{\lambda'}(\mathcal{H}\sigma)}. \tag{3.2-7}$$

Insertion of this expression into Eq. 3.1-3 yields the familiar expression for the quantum mechanical cross section for the collision of two rigid spheres. This is to be expected, since if we set δ equal to zero our model of the loaded sphere becomes simply an ordinary sphere. The presence of the product $\delta_{\ell^a \bar{\ell}^a} \; \delta_{\ell^b \bar{\ell}^b}$ indicates that this is an elastic cross section; that is, there is no change of internal state in the course of the collision. This is also expected, since the only mechanism for the change of internal state in a loaded sphere is due to the fact that the sphere does not rotate about its geometrical center. As δ approaches zero the means of exchange of internal energy upon collision also vanishes.

The expression for $I(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | J)_1$ is obtained by inserting the coefficient of δ/σ in Eq. 3.1-6 into Eq. 3.1-4. When we examine the expression for $f(\bar{p} \angle p)_1$, Eq. 2.4-4, we note that every term of $I(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | J)_1$ will contain either $S^{1\bar{\ell}^a}_{\ell^a 00} \; \delta_{\ell^a \bar{\ell}^a}$ or $S^{1\bar{\ell}^b}_{\ell^b 00} \; \delta_{\ell^b \bar{\ell}^b}$. But both of these products are zero; we therefore conclude that

$$I(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | J)_1 = 0 \qquad (3.2\text{-}8)$$

We now come to the main task of this chapter.

Section 3.3 <u>The Evaluation of $I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$ - The Elastic Part</u>

In Eq. 3.2-7 we showed that $I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_0$ is the cross section expansion coefficient for the rigid sphere. In Eq. 3.2-8 we see that terms of the first power of δ/σ make no contribution to the cross section. Therefore, the first nonvanishing correction to the rigid sphere cross section is of the order of $(\delta/\sigma)^2$. It is in this term that we shall see the possibility of inelastic collisions, and we shall discover how selection rules for such collisions arise. These inelastic collisions give rise to the quantity known as the relaxation time, which will be evaluated in Chapter VI.

We note from Eq. 3.1-6 that the coefficient of $(\delta/\sigma)^2$ contains three terms,

$$f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}L\ell^a\ell^b\ell\lambda)_0\, f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}'L'\ell^a\ell^b\ell\lambda')_2^*, \qquad (3.3\text{-}1)$$

$$f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}L\ell^a\ell^b\ell\lambda)_1\, f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}'L'\ell^a\ell^b\ell\lambda')_1^*, \qquad (3.3\text{-}2)$$

and

$$f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}L\ell^a\ell^b\ell\lambda)_2\, f(\bar{\ell}^a\bar{\ell}^b\bar{\ell}\bar{\lambda}'L'\ell^a\ell^b\ell\lambda')_0^*. \qquad (3.3\text{-}3)$$

The first and third of these contain $f(\bar{p}\,l\,p)_0$, and therefore give rise to elastic terms only in the cross section. Also, it is easy to show that the results obtained from inserting Eqs. 3.3-1 and 3.3-3 into Eq. 3.1-4 are just complex conjugates of each other. The middle term, Eq. 3.3-2, is the most interesting -- it gives rise to the term in the cross section describing an inelastic scattering process. The inelastic contribution to the cross section has been obtained by Gioumousis and Curtiss[28] for the special case that $\bar{\ell}^{a}$, $\bar{\ell}^{b}$, and ℓ^{b} are zero and ℓ^{a} is one. We now introduce two new symbols. The elastic cross section $I_{el}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2$ is the sum of the results of inserting Eqs. 3.3-1 and 3.3-3 into Eq. 3.1-4. The inelastic cross section $I_{inel}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2$ is the term arising from Eq. 3.3-2. It then follows that

$$I(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2 = I_{el}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2$$

$$+ I_{inel}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2 . \qquad (3.3\text{-}4)$$

Proceeding now to the evaluation of $I_{el}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2$ we write

$$I_{\ell\ell}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = \frac{1}{(2\ell^a+1)(2\ell^b+1)}$$

$$\times \frac{1}{\mathcal{K}}\,\delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}\sum_{\substack{\ell\lambda\lambda' \\ \bar{\lambda}'LL'}} i^{\,1-\bar{\lambda}'}\,(2L+1)(2L'+1)$$

$$\times(2\lambda+1)(2\bar{\lambda}'+1)\,S^{\lambda\lambda'}_{J00}\,S^{\lambda\bar{\lambda}'}_{J00}\,W(L\lambda L'\lambda'\ell J)$$

$$\times W(L\lambda L'\bar{\lambda}'\ell J)\,\frac{\hbar_\lambda(\mathcal{K}\sigma)}{h_\lambda(\mathcal{K}\sigma)}\,f(\ell^a\ell^b\ell\bar{\lambda}'L'\ell^a\ell^b\ell\lambda')^*_2$$

$$+\ C.C. \tag{3.3-5}$$

In writing the above equation we have inserted the expression for $f(\bar{p}Lp)_0$, Eq. 2.3-14, into Eq. 3.1-4 and have carried out the sums over $\bar{\ell}$ and $\bar{\lambda}$. The letters $C.C.$ denote the complex conjugate; the complex conjugate of the entire expression is to be added. The summation over L may now be carried out with the help of Eq. A.1-12 and we find that

$$I_{\ell\ell}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2 = \frac{1}{(2\ell^{a}+1)(2\ell^{b}+1)} \delta_{\ell^{a}\bar{\ell}^{a}} \delta_{\ell^{b}\bar{\ell}^{b}}$$

$$\times \frac{1}{\mathcal{H}} \sum_{\ell\lambda\lambda' L'} i^{1-\lambda'} (2L'+1)(2\lambda+1)(S_{500}^{\lambda\lambda'})^2 \frac{j_\lambda(\mathcal{H}\sigma)}{h_\lambda(\mathcal{H}\sigma)}$$

$$\times f(\ell^{a}\ell^{b}\ell\lambda' L'\ell^{a}\ell^{b}\ell\lambda')_2^* + \text{C.C.} \qquad (3.3\text{-}6)$$

It will be remembered from Chapter II that $f(p\,L\,p)_2$ consists of three parts labeled A, B, and C, and that A and B were further divided. We now insert these parts of $f(p\,L\,p)_2$ one at a time into Eq. 3.3-6, and affix a subscript to $I_{\ell\ell}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2$ to denote the part of $f(p\,L\,p)_2$ which has been used. For example, $I_{\ell\ell,B_3}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2$ denotes the result obtained by substituting the expression for B_3, Eq. 2.5-20, into Eq. 3.3-6. The total expression for $I_{\ell\ell}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2$ is then of the form

$$I_{\ell\ell}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2 = \sum_{j=1}^{5} I_{\ell\ell,A_j}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2$$

$$+ \sum_{j=1}^{3} I_{\ell\ell,B_j}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2 + I_{\ell\ell,C}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2 .$$

(3.3-7)

This equation states that $I_{\ell\ell}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)$ is the sum of nine terms. We now compute these parts individually.

The expression for $A_1(pLp)$ is given in Eq. 2.5-3. Hence

$$I_{\ell\ell,A_1}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = -\frac{2i}{3\varkappa^3\sigma}\frac{1}{(2\ell^a+1)(2\ell^b+1)}$$

$$\times\delta_{\ell^a\bar{\ell}^a}\delta_{\ell^b\bar{\ell}^b}\sum_{\lambda\lambda'\ell L'}(2L'+1)(2\lambda+1)\left(S^{\lambda\lambda'}_{J00}\right)^2$$

$$\times\frac{1}{h^{*2}_{\lambda'}(\varkappa\sigma)}\frac{f_\lambda(\varkappa\sigma)}{h_\lambda(\varkappa\sigma)}\Delta(\ell^a\ell^b\ell)\Delta(\ell\lambda' L') + C.C. \tag{3.3-8}$$

We are now free to carry out the sum over ℓ and L' by means of Eq. 3.2-6. Putting this result into Eq. 3.3-8 and writing out explicitly the complex conjugate term we find

$$I_{\ell\ell,A_1}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = \delta_{\ell^a\bar{\ell}^a}\delta_{\ell^b\bar{\ell}^b}\frac{2i}{3\varkappa^3\sigma}$$

$$\times\sum_{\lambda\lambda'}(2\lambda+1)(2\lambda'+1)\left(S^{\lambda\lambda'}_{J00}\right)^2\left[\frac{1}{h^2_{\lambda'}(\varkappa\sigma)}\frac{f_\lambda(\varkappa\sigma)}{h^*_\lambda(\varkappa\sigma)}\right.$$

$$\left.-\frac{1}{h^{*2}_{\lambda'}(\varkappa\sigma)}\frac{f_\lambda(\varkappa\sigma)}{h_\lambda(\varkappa\sigma)}\right]. \tag{3.3-9}$$

In order to obtain $I_{ee,A_2}(\bar{e}^a\bar{e}^b e^a e^b|J)_2$ we insert Eq. 2.5-5 into Eq. 3.3-6. This gives

$$I_{ee,A_2}(\bar{e}^a\bar{e}^b e^a e^b|J)_2 = \frac{1}{\sqrt{2e^a+1}\,(2e^b+1)}$$

$$\times\delta_{e^a\bar{e}^a}\,\delta_{e^b\bar{e}^b}\,\frac{i}{3\kappa^3\sigma}\sum_{e\lambda\lambda' L'}(2L'+1)(2e+1)(2\lambda+1)$$

$$\times\sqrt{2\lambda'+1}\,\left(S^{\lambda\lambda'}_{J00}\right)^2 S^{2e^a}_{e^a00}\,S^{2\lambda'}_{\lambda'00}$$

$$\times W(2e^a e e^b e^a e)\,W(e2L'\lambda' e\lambda')$$

$$\times\frac{1}{h^{*2}_{\lambda'}(\kappa\sigma)}\,\frac{j_\lambda(\kappa\sigma)}{h_\lambda(\kappa\sigma)} + \text{C.C.} \qquad (3.3\text{-}10)$$

From Eqs. A.1-12 and A.1-13 we see that

$$\sum_{L'}(2L'+1)\,W(e2L'\lambda' e\lambda') = \sum_{L'}(-1)^{L'+e+\lambda'}$$

$$\times(2L'+1)\,W(e\lambda' e\lambda' L'2) = \sqrt{(2e+1)(2\lambda'+1)}$$

$$\times\sum_{L'}(2L'+1)\,W(e\lambda' e\lambda' L'2)\,W(e\lambda' e\lambda' L'0) = 0. \qquad (3.3\text{-}11)$$

Hence

$$I_{el,A_2}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2 = 0. \tag{3.3-12}$$

From Eqs. 2.5-8 and 2.5-9 we have that $A_3(p\,l\,p)$ and $A_4(p\,l\,p)$ are equal to zero. Hence

$$I_{el,A_3}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2 = 0, \tag{3.3-13}$$

and

$$I_{el,A_4}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2 = 0. \tag{3.3-14}$$

In the same manner that we showed I_{el,A_2} is equal to zero we can show that

$$I_{el,A_5}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2 = 0. \tag{3.3-15}$$

This then completes the evaluation of that part of the elastic cross section due to the term $A(p\,l\,p)$ in the scattering amplitude.

The expression for $B_1(p\,l\,p)$ is given by Eq. 2.5-17. Upon insertion of this quantity into Eq. 3.3-6 we obtain

$$I_{ee,B_1}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = -\frac{i}{\sqrt{2\ell^a+1}\,(2\ell^b+1)}\frac{\delta_{\ell^a\bar{\ell}^a}\delta_{\ell^b\bar{\ell}^b}}{\varkappa^3\sigma}$$

$$\times\sum_{\substack{\ell\lambda\lambda'\\ L'q}}(-1)^q(2L'+1)(2\lambda+1)(2\ell+1)\sqrt{2\lambda'+1}$$

$$\times\left(S^{\lambda\lambda'}_{J00}\right)^2\left(S^{\ell\ell}_{q00}\right)^2 S^{q\ell^a}_{\ell^a00}\,S^{q\lambda'}_{\lambda'00}$$

$$\times W(\ell q L'\lambda'\ell\lambda')\,W(q\ell^a\ell\ell^b\ell^a\ell)$$

$$\times\frac{1}{h^{*2}_{\lambda'}(\varkappa\sigma)}\frac{j_\lambda(\varkappa\sigma)}{h_\lambda(\varkappa\sigma)} + \mathrm{C.C.} \qquad (3.3\text{-}16)$$

Now from Eqs. A.1-19 and A.1-16 we see that

$$(-1)^q\,W(\ell q L'\lambda'\ell\lambda') = (-1)^{L'+\ell+\lambda'}\,W(\lambda'\ell\lambda'\ell L'q), \qquad (3.3\text{-}17)$$

and from Eq. A.1-13 that

$$(-1)^{\ell+\lambda'+L'} = \sqrt{(2\ell+1)(2\lambda'+1)}\,W(\lambda'\ell\lambda'\ell L'0). \qquad (3.3\text{-}18)$$

Hence by carrying out the sum over L' and q, and utilizing Eq. A.1-10, we obtain

$$I_{\ell\ell,B_1}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = -\frac{i}{3\sqrt{2\ell^a+1}\,(2\ell^b+1)}$$

$$\times\frac{1}{\varkappa^3\sigma}\,\delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}\sum_{\ell\lambda\lambda'}(2\lambda+1)(2\lambda'+1)(2\ell+1)^{\frac{3}{2}}$$

$$\times\left(S^{\lambda\lambda'}_{J00}\right)^2\, W(0\ell^a\ell\ell^b\ell^a\ell)\,\frac{1}{h^{*2}_{\lambda'}(\varkappa\sigma)}$$

$$\times\frac{j_\lambda(\varkappa\sigma)}{h_\lambda(\varkappa\sigma)} + \text{C.C.} \qquad (3.3\text{-}19)$$

Then, by making use of Eq. A.1-13 we obtain the result

$$I_{\ell\ell,B_1}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = \frac{i}{3\varkappa^3\sigma}\,\delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}$$

$$\times\sum_{\lambda\lambda'}(2\lambda+1)(2\lambda'+1)\left(S^{\lambda\lambda'}_{J00}\right)^2\left[\frac{1}{h^{2}_{\lambda'}(\varkappa\sigma)}\right.$$

$$\left.\times\frac{j_\lambda(\varkappa\sigma)}{h^*_\lambda(\varkappa\sigma)} - \frac{1}{h^{*2}_{\lambda'}(\varkappa\sigma)}\,\frac{j_\lambda(\varkappa\sigma)}{h_\lambda(\varkappa\sigma)}\right]. \qquad (3.3\text{-}20)$$

Since $B_2(p\,l\,p)$ is equal to zero, Eq. 2.5-19, it follows that

$$I_{\ell\ell,B_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = 0. \qquad (3.3\text{-}21)$$

In order to complete the evaluation of $I_{\ell\ell,B}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$ we require $I_{\ell\ell,B_3}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$. However, it is easy to show that

$$I_{\ell\ell,B_3}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = I_{\ell\ell,B_1}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 . \qquad (3.3\text{-}22)$$

By noticing the similarity among the expressions thus far obtained we may summarize by writing

$$I_{\ell\ell,A+B}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = \sum_{j=1}^{5} I_{\ell\ell,A_j}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$$

$$+ \sum_{j=1}^{3} I_{\ell\ell,B_j}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 =$$

$$\times \delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}\,\frac{4i}{3\kappa^3\sigma}\sum_{\lambda\lambda'}(2\lambda+1)(2\lambda'+1)\left(S_{J00}^{\lambda\lambda'}\right)^2$$

$$\times\left[\frac{1}{h_{\lambda'}^{2}(\kappa\sigma)}\,\frac{j_\lambda(\kappa\sigma)}{h_\lambda^{*}(\kappa\sigma)} - \frac{1}{h_{\lambda'}^{*2}(\kappa\sigma)}\,\frac{j_\lambda(\kappa\sigma)}{h_\lambda(\kappa\sigma)}\right].$$

(3.3-23)

In order to complete the evaluation of the elastic part of the cross section, we now calculate $I_{el,c}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$. This is obtained by substituting Eq. 2.5-22 into Eq. 3.3-6. When we make this substitution we get

$$I_{el,c}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = -\frac{1}{(2\ell^a+1)(2\ell^b+1)}\delta_{\ell^a\bar{\ell}^a}\delta_{\ell^b\bar{\ell}^b}$$

$$\times\frac{i}{\mathcal{H}^3}\sum_{\substack{\ell\lambda\lambda'\iota' \\ \tilde{\lambda}\tilde{\ell}\tilde{\ell}^a\tilde{\ell}^b\tilde{\ell}}}\Big\{\tilde{\mathcal{H}}(2\iota'+1)(2\lambda+1)(2\lambda'+1)(2\ell+1)(2\tilde{\ell}+1)$$

$$\times(S^{\lambda\lambda'}_{J00})^2\quad(S^{1\lambda'}_{\tilde{\lambda}00})^2 W^2(\ell 1\iota'\tilde{\lambda}\tilde{\ell}\lambda')$$

$$\times\frac{j_\lambda(\mathcal{H}\sigma)}{h_\lambda(\mathcal{H}\sigma)}\frac{1}{h^{*2}_{\lambda'}(\mathcal{H}\sigma)}\frac{h'^{*}_{\tilde{\lambda}}(\tilde{\mathcal{H}}\sigma)}{h^{*}_{\tilde{\lambda}}(\tilde{\mathcal{H}}\sigma)}\Big[(2\ell^b+1)(S^{1\ell^b}_{\tilde{\ell}^b00})^2$$

$$\times\delta_{\ell^a\tilde{\ell}^a}W^2(1\ell^b\tilde{\ell}\ell^a\tilde{\ell}^b\ell)+(2\ell^a+1)(S^{1\ell^a}_{\tilde{\ell}^a00})^2$$

$$\times\delta_{\ell^b\tilde{\ell}^b}W^2(1\ell^a\tilde{\ell}\ell^b\tilde{\ell}^a\ell)\Big]\Big\}\quad + C.C. \qquad (3.3\text{-}24)$$

The only terms in this expression containing ι' are $(2\iota'+1)$ and $W^2(\ell 1\iota'\tilde{\lambda}\tilde{\ell}\lambda')$. We may therefore carry out this sum to obtain 1/3. Next the sum over ℓ is carried out using Eq. A.1-12. This results in

$$I_{ee,c}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = -\frac{1}{(2\ell^a+1)(2\ell^b+1)}$$

$$\times \delta_{\ell^a\tilde{\ell}^a}\delta_{\ell^b\tilde{\ell}^b}\frac{i}{3\mathcal{H}^3}\sum_{\substack{\lambda\lambda'\tilde{\lambda}\\ \tilde{\ell}^a\tilde{\ell}^b\tilde{\ell}}}\Big\{\tilde{\mathcal{H}}(2\lambda+1)(2\lambda'+1)(2\tilde{\ell}+1)$$

$$\times\left(S^{\lambda\lambda'}_{J00}\right)^2\left(S^{1\lambda'}_{\tilde{\lambda}00}\right)^2\frac{1}{h^{*2}_{\lambda'}(\mathcal{H}\sigma)}\frac{h^{\prime *}_{\tilde{\lambda}}(\tilde{\mathcal{H}}\sigma)}{h^{*}_{\tilde{\lambda}}(\tilde{\mathcal{H}}\sigma)}\frac{j_\lambda(\mathcal{H}\sigma)}{h_\lambda(\mathcal{H}\sigma)}$$

$$\times\Bigg[\frac{2\ell^a+1}{2\tilde{\ell}^a+1}\left(S^{1\ell^a}_{\tilde{\ell}^a00}\right)^2\Delta(\tilde{\ell}\tilde{\ell}^a\ell^b)\,\delta_{\ell^b\tilde{\ell}^b}+\frac{2\ell^b+1}{2\tilde{\ell}^b+1}$$

$$\times\left(S^{1\ell^b}_{\tilde{\ell}^b00}\right)^2\Delta(\tilde{\ell}\ell^a\tilde{\ell}^b)\,\delta_{\ell^a\tilde{\ell}^a}\Bigg]\Bigg\}+C.C. \qquad (3.3\text{-}25)$$

We now carry out the sum over $\tilde{\ell}$ by using Eq. 3.2-5. The final result is

$$I_{ee,c}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = \delta_{\ell^a\tilde{\ell}^a}\delta_{\ell^b\tilde{\ell}^b}\frac{i}{3\mathcal{H}^3}$$

$$\times\sum_{\substack{\lambda\lambda'\tilde{\lambda}\\ \tilde{\ell}^a\tilde{\ell}^b}}\Big\{\tilde{\mathcal{H}}\Big[\left(S^{1\ell^a}_{\tilde{\ell}^a00}\right)^2\delta_{\ell^b\tilde{\ell}^b}+\left(S^{1\ell^b}_{\tilde{\ell}^b00}\right)^2\delta_{\ell^a\tilde{\ell}^a}\Big]$$

$$\times(2\lambda+1)(2\lambda'+1)\left(S^{\lambda\lambda'}_{J00}\right)^2\left(S^{1\lambda'}_{\tilde{\lambda}00}\right)^2$$

$$\times\left[\frac{h'_{\tilde{\lambda}}(\tilde{\varkappa}\sigma)}{h_{\tilde{\lambda}}(\tilde{\varkappa}\sigma)}\frac{1}{h^2_{\lambda'}(\varkappa\sigma)}\frac{j_{\lambda}(\varkappa\sigma)}{h^*_{\lambda}(\varkappa\sigma)}-\frac{h'^*_{\tilde{\lambda}}(\tilde{\varkappa}\sigma)}{h^*_{\tilde{\lambda}}(\tilde{\varkappa}\sigma)}\right.$$

$$\left.\times\frac{1}{h^{*2}_{\lambda'}(\varkappa\sigma)}\frac{j_{\lambda}(\varkappa\sigma)}{h_{\lambda}(\varkappa\sigma)}\right]\Bigg\}. \qquad (3.3\text{-}26)$$

We have now obtained all the contributions to the elastic cross section. They are given by Eqs. 3.2-7, 3.3-23 and 3.3-26.

Section 3.4 <u>The Evaluation of $I(\bar{\ell}a_{\bar{\ell}}b_{\ell}a_{\ell}b|J)_2$</u> --

<u>The Inelastic Part</u>

We now evaluate the only remaining part of the cross section, the inelastic part. This arises when we substitute Eq. 3.3-2 into Eq. 3.1-4. When we use the explicit form of $f(\bar{p}Lp)$, as given in Eq. 2.4-4 we obtain

$$I_{\mathrm{inel}}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | J)_2 = \frac{1}{(2\ell^a+1)(2\ell^b+1)} \frac{1}{\varkappa \bar{\varkappa}^3 \sigma^2}$$

$$\times \sum_{\substack{\bar{\ell}\bar{\lambda}\ell\lambda \\ \bar{\lambda}'\lambda' L L'}} i^{\bar{\lambda}-\bar{\lambda}'+\lambda'-\lambda} (-1)^{\ell+\bar{\ell}} (2L+1)(2L'+1)$$

$$\times \sqrt{(2\bar{\lambda}+1)(2\bar{\lambda}'+1)} \; (2\lambda+1)(2\lambda'+1)(2\ell+1)(2\bar{\ell}+1)$$

$$\times S^{\bar{\lambda}\bar{\lambda}'}_{J00} \; S^{\lambda\lambda'}_{J00} \; S^{1\lambda'}_{\bar{\lambda}'00} \; S^{1\lambda}_{\bar{\lambda}00} \, W(L\lambda L'\lambda'\ell J)$$

$$\times W(\bar{\ell} 1 L \lambda \ell \bar{\lambda}) \, W(\bar{\ell} 1 L' \lambda' \ell \bar{\lambda}') \, W(L\bar{\lambda}L'\bar{\lambda}'\bar{\ell} J)$$

$$\times \Big[(2\ell^a+1)\big(S^{1\bar{\ell}^a}_{\ell^a 00}\big)^2 \delta_{\ell^b \bar{\ell}^b} W^2(1\bar{\ell}^a \ell \ell^b \ell^a \bar{\ell})$$

$$+ (2\ell^b+1)\big(S^{1\bar{\ell}^b}_{\ell^b 00}\big)^2 \delta_{\ell^a \bar{\ell}^a} W^2(1\bar{\ell}^b \ell \ell^a \ell^b \bar{\ell}) \Big]$$

$$\times \frac{1}{h_\lambda(\varkappa\sigma) h_{\bar{\lambda}}(\bar{\varkappa}\sigma) h^*_{\lambda'}(\varkappa\sigma) h^*_{\bar{\lambda}'}(\bar{\varkappa}\sigma)} . \tag{3.4-1}$$

We now use Eq. A.1-14 in the form

$$\sum_{L'} (2L'+1) W(L\lambda L'\lambda' \ell J) W(L\bar{\lambda}L'\bar{\lambda}'\bar{\ell}J) W(\bar{\ell}1L'\lambda'\ell\bar{\lambda}')$$

$$= (-1)^{\ell+\bar{\ell}+\lambda'+\bar{\lambda}'} W(J\lambda\bar{\lambda}'1\lambda'\bar{\lambda}) W(L\lambda\bar{\ell}1\ell\bar{\lambda}).$$

(3.4-2)

The sum over L then gives 1/3. Thus

$$I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = \frac{1}{(2\ell^a+1)(2\ell^b+1)} \frac{1}{3\varkappa\bar{\varkappa}^3\sigma^2}$$

$$\times \sum_{\substack{\bar{\ell}\ell\lambda \\ \lambda'\bar{\lambda}\bar{\lambda}'}} i^{\bar{\lambda}-\bar{\lambda}'+\lambda'-\lambda} (-1)^{\lambda'+\bar{\lambda}'} \sqrt{(2\bar{\lambda}+1)(2\bar{\lambda}'+1)}$$

$$\times (2\lambda+1)(2\lambda'+1) S^{1\lambda'}_{\bar{\lambda}'00} S^{1\lambda}_{\bar{\lambda}00} S^{\lambda\lambda'}_{J00} S^{\bar{\lambda}\bar{\lambda}'}_{J00}$$

$$\times W(J\lambda\bar{\lambda}'1\lambda'\bar{\lambda})$$

$$\times \Big[(2\ell^a+1)(S^{1\bar{\ell}^a}_{\ell^a00})^2 \delta_{\ell^b\bar{\ell}^b} W^2(1\bar{\ell}^a\ell\ell^b\ell^a\bar{\ell})$$

$$+ (2\ell^b+1)(S^{1\bar{\ell}^b}_{\ell^b00})^2 \delta_{\ell^a\bar{\ell}^a} W^2(1\bar{\ell}^b\ell\ell^a\ell^b\bar{\ell}) \Big]$$

$$\times \frac{1}{h_\lambda(\varkappa\sigma) h_{\bar{\lambda}}(\bar{\varkappa}\sigma) h^*_{\lambda'}(\varkappa\sigma) h^*_{\bar{\lambda}'}(\bar{\varkappa}\sigma)}.$$

(3.4-3)

The final form is obtained by carrying out the sums over ℓ and $\bar{\ell}$ by the use of Eqs. A.1-12 and 3.2-5. We then have

$$I_{inel}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | J)_2 = \frac{2J+1}{3\mathcal{H}\bar{\mathcal{H}}^3 \sigma^2}$$

$$\times \left\{ \left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2 \delta_{\ell^b \bar{\ell}^b} + \left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2 \delta_{\ell^a \bar{\ell}^a} \right\}$$

$$\times \sum_{\lambda\lambda'\bar{\lambda}\bar{\lambda}'} (-1)^{1+J+\lambda+\bar{\lambda}'} \, i^{\bar{\lambda}-\bar{\lambda}'+\lambda'-\lambda} \sqrt{(2\lambda'+1)(2\bar{\lambda}+1)} \, (2\lambda+1)$$

$$\times S^{\lambda J}_{\lambda' 00} \, S^{\bar{\lambda} J}_{\bar{\lambda}' 00} \, S^{\lambda 1}_{\bar{\lambda} 00} \, S^{\lambda' 1}_{\bar{\lambda}' 00} \quad W(\lambda \bar{\lambda} \lambda' \bar{\lambda}' \, 1 \, J)$$

$$\times \frac{1}{h_\lambda(\mathcal{H}\sigma) \, h_{\bar{\lambda}}(\bar{\mathcal{H}}\sigma) \, h^{*}_{\lambda'}(\mathcal{H}\sigma) \, h^{*}_{\bar{\lambda}'}(\bar{\mathcal{H}}\sigma)} \, . \qquad (3.4\text{-}4)$$

For any given value of J the above fourfold sum can be reduced to a single sum over λ, since for any λ the Wigner coefficients restrict the number of possible values of λ', $\bar{\lambda}$, and $\bar{\lambda}'$ (See Appendix III). The presence of the factor

$$\left\{ \left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2 \delta_{\ell^b \bar{\ell}^b} + \left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2 \delta_{\ell^a \bar{\ell}^a} \right\} \qquad (3.4\text{-}5)$$

means that one of the molecules changes its internal state while the other does not, and that the change in the quantum number ℓ^a or ℓ^b is equal to plus or minus one. This selection rule, which holds for all values of J, arises from the fact that this is the second term in an expansion of $I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$ in powers of δ/σ. Presumably, larger transitions would be allowed in successive terms.

We now have an exact quantum mechanical expression for the cross section for the collision of two loaded sphere molecules through the second power in δ/σ. In the following chapter, we shall calculate certain moments of the cross section which are necessary for the calculation of the transport coefficients.

CHAPTER IV

MOMENTS OF THE CROSS SECTION

In Chapter III we derived an exact quantum mechanical expression for the cross section for the collision of two loaded spheres. Our goal is to calculate the transport coefficients for a gas made up of such molecules. In this chapter we shall calculate several quantities related to the cross section which are necessary for such a calculation.

Section 4.1 The Evaluation of $Q^{(1)}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_0$ and $Q^{(2)}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_0$

In the classical theory of the transport phenomena of spherically symmetric molecules, certain moments of the cross section $Q^{(\ell)}(g)$ are defined by

$$Q^{(\ell)}(g) = 2\pi \int_0^{\pi} (1-\cos^{\ell}\chi)\, I(g,\chi) \sin\chi \, d\chi \, . \tag{4.1-1}$$

Here g is the relative velocity of the molecules before (and after) collision, and $I(g,\chi)$ is the cross section for scattering through an angle χ. If we expand $I(g,\chi)$ in a series of Legendre polynomials,

$$I(g,\chi) = \sum_{\ell=0}^{\infty} I_{\ell}(g)\, P_{\ell}(\cos\chi), \tag{4.1-2}$$

we find that

$$Q^{(1)}(g) = 4\pi\left[I_0(g) - \frac{1}{3} I_1(g)\right], \tag{4.1-3}$$

and

$$Q^{(2)}(g) = \frac{8\pi}{3}\left[I_0(g) - \frac{1}{5} I_2(g)\right]. \tag{4.1-4}$$

In an analogous manner we define $Q^{(1)}$ and $Q^{(2)}$ for our loaded sphere molecules by

$$Q^{(1)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b) = 4\pi\left[I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|0) - \frac{1}{3} I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|1)\right], \tag{4.1-5}$$

and

$$Q^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b) = \frac{8\pi}{3}\left[I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|0) - \frac{1}{5} I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|2)\right]. \tag{4.1-6}$$

These two quantities, along with the inelastic parts of the cross section expansion coefficients $I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$ for J equal to 0, 1, and 2, are needed for the calculation of the transport coefficients. Explicit formulas for these coefficients are given in Chapter VI.

When the expansion of $I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)$ in powers of δ/σ, Eq. 3.1-5, is inserted into Eq. 4.1-5 we obtain a similar expansion of $\mathcal{Q}^{(1)}$,

$$\mathcal{Q}^{(1)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}) = \sum_{j=0}^{\infty} \mathcal{Q}^{(1)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_j \left(\frac{\delta}{\sigma}\right)^j , \tag{4.1-7}$$

where

$$\mathcal{Q}^{(1)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_j = 4\pi \left[I(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|0)_j - \frac{1}{3} I(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|1)_j \right]. \tag{4.1-8}$$

The procedure for $\mathcal{Q}^{(2)}$ is identical. From Eq. 3.1-5 we see that the quantities $I(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_0$ are the cross section expansion coefficients in the case δ equals zero, that is, in the case that the loaded sphere becomes an ordinary sphere. Hence $\mathcal{Q}^{(1)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_0$ and $\mathcal{Q}^{(2)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_0$, which we calculate in this section, are the $\mathcal{Q}^{(1)}$ and $\mathcal{Q}^{(2)}$ for rigid spheres of diameter σ .

The expression for $I(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_0$ is given by Eq. 3.2-7. We introduce the phase shift for rigid spheres, η_λ , defined by

$$\tan \eta_\lambda(\kappa\sigma) = \frac{j_\lambda(\kappa\sigma)}{n_\lambda(\kappa\sigma)} ; \tag{4.1-9}$$

where j_λ and n_λ are the spherical Bessel and Neumann functions. From this definition it is easy to show that

$$\frac{\gamma_\lambda(\mathcal{H}\sigma)}{h_\lambda(\mathcal{H}\sigma)} = \frac{1}{2}\left[1 - e^{2i\eta_\lambda(\mathcal{H}\sigma)}\right]. \qquad (4.1\text{-}10)$$

When this expression is substituted into Eq. 3.2-7 we find that

$$I(\bar{\ell}^a\bar{\ell}^b\,\ell^a\ell^b|0)_0 = \delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}\,\frac{1}{4\mathcal{H}^2}\sum_\lambda(2\lambda+1)$$

$$\times(1-e^{2i\eta_\lambda})(1-e^{-2i\eta_\lambda}) = \delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}\,\frac{1}{\mathcal{H}^2}$$

$$\times\sum_\lambda(2\lambda+1)\sin^2\eta_\lambda, \qquad (4.1\text{-}11)$$

and

$$I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|1)_0 = \delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}\,\frac{3}{4\mathcal{H}^2}$$

$$\times\sum_{\lambda\lambda'}(2\lambda+1)(S^{\lambda 1}_{\lambda' 0 0})^2(1-e^{2i\eta_\lambda})(1-e^{-2i\eta_{\lambda'}}). \qquad (4.1\text{-}12)$$

Due to the presence of the factor $(S^{\lambda 1}_{\lambda' 0 0})^2$ the index λ' is restricted to the values $\lambda+1$ and $\lambda-1$. Hence

$$I(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | 1)_0 = \delta_{\ell^a \bar{\ell}^a} \delta_{\ell^b \bar{\ell}^b} \frac{3}{4\mathcal{H}^2}$$

$$\times \sum_{\lambda} (2\lambda+1) \Big[(S^{\lambda 1}_{\lambda+1\,0\,0})^2 (1-e^{2i\eta_\lambda})(1-e^{-2i\eta_{\lambda+1}})$$

$$+ (S^{\lambda 1}_{\lambda-1\,0\,0})^2 (1-e^{2i\eta_\lambda})(1-e^{-2i\eta_{\lambda-1}}) \Big]. \qquad (4.1\text{-}13)$$

From tables in Condon and Shortley[32] we find that

$$(S^{\lambda 1}_{\lambda+1\,0\,0})^2 = \frac{\lambda+1}{2\lambda+1}, \quad (S^{\lambda 1}_{\lambda-1\,0\,0})^2 = \frac{\lambda}{2\lambda+1}. \qquad (4.1\text{-}14)$$

We substitute these into Eq. 4.1-12 and change the index λ to $\lambda+1$ in the second term. This gives

$$I(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | 1)_0 = \delta_{\ell^a \bar{\ell}^a} \delta_{\ell^b \bar{\ell}^b} \frac{3}{4\mathcal{H}^2}$$

$$\times \sum_{\lambda} (\lambda+1) \Big[(1-e^{2i\eta_\lambda})(1-e^{-2i\eta_{\lambda+1}})$$

$$+ (1-e^{2i\eta_{\lambda+1}})(1-e^{-2i\eta_\lambda}) \Big]. \qquad (4.1\text{-}15)$$

When the exponentials are expressed in terms of trigonometric functions we find that

$$I(\bar{e}^a \bar{e}^b e^a e^b | 1)_0 = \delta_{e^a \bar{e}^a} \delta_{e^b \bar{e}^b} \frac{3}{\mathcal{H}^2} \sum_{\lambda} \Big\{ (\lambda+1)$$

$$\times \left[\sin^2 \eta_\lambda + \sin^2 \eta_{\lambda+1} - \sin^2 (\eta_{\lambda+1} - \eta_\lambda) \right] \Big\}. \qquad (4.1\text{-}16)$$

Finally, by lowering the index λ by one in the $\sin^2 \eta_{\lambda+1}$ term, we obtain

$$I(\bar{e}^a \bar{e}^b e^a e^b | 1)_0 = \delta_{e^a \bar{e}^a} \delta_{e^b \bar{e}^b} \frac{3}{\mathcal{H}^2} \sum_{\lambda} \Big[(2\lambda+1) \sin^2 \eta_\lambda$$

$$- (\lambda+1) \sin^2 (\eta_{\lambda+1} - \eta_\lambda) \Big]. \qquad (4.1\text{-}17)$$

By performing similar manipulations we find that

$$I(\bar{e}^a \bar{e}^b e^a e^b | 2)_0 = \delta_{e^a \bar{e}^a} \delta_{e^b \bar{e}^b} \frac{5}{\mathcal{H}^2}$$

$$\times \sum_{\lambda} \left[(2\lambda+1) \sin^2 \eta_\lambda - \frac{3}{2} \frac{(\lambda+1)(\lambda+2)}{(2\lambda+3)} \sin^2 (\eta_{\lambda+2} - \eta_\lambda) \right].$$

$$(4.1\text{-}18)$$

We now combine these results according to Eqs. 4.1-5 and 4.1-6, which gives

$$Q^{(1)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_0 = \delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}\,\frac{4\pi}{\varkappa^2}\sum_{\lambda}(\lambda+1)\sin^2(\eta_{\lambda+1}-\eta_{\lambda}) \,, \tag{4.1-19}$$

and

$$Q^{(2)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_0 = \delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}\,\frac{4\pi}{\varkappa^2}\sum_{\lambda}\frac{(\lambda+1)(\lambda+2)}{(2\lambda+3)}\sin^2(\eta_{\lambda+2}-\eta_{\lambda}) . \tag{4.1-20}$$

These are the well known expressions for $Q^{(1)}$ and $Q^{(2)}$ for rigid spheres[33].

In Chapter III we showed that $I(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_1$ is equal to zero. Hence $Q^{(1)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_1$ and $Q^{(2)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_1$ are also equal to zero.

The derivation of these formulas has been given in some detail, since exactly the same techniques will be used to express the correction terms to the rigid sphere Q's in terms of the rigid sphere phase shifts.

Section 4.2 The Evaluation of $Q^{(1)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_2$ and $Q^{(2)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_2$ The Elastic Part.

As we have done in the previous chapter, we divide $Q^{(1)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_2$ and $Q^{(2)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_2$ into separate parts corresponding to the parts into which $I(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2$ has been divided (see Eqs. 3.3-4 and 3.3-7), and we affix a subscript to $\mathcal{Q}$ to label the separate parts.

We begin by evaluating $\mathcal{Q}^{(1)}_{\ell\ell,C}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2$. The expression for $\mathcal{I}_{\ell\ell,C}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$ is given by Eq. 3.3-26. It is convenient to express this quantity entirely in terms of rigid sphere phase shifts. This can be done by differentiating both sides of Eq. 4.1-10 with respect to $\mathcal{H}\sigma$ and using Eq. 2.3-16 to obtain

$$\frac{1}{h_\lambda^2(\mathcal{H}\sigma)} = \mathcal{H}^2\sigma^2\eta_\lambda'(\mathcal{H}\sigma)e^{2i\eta_\lambda(\mathcal{H}\sigma)} . \qquad (4.2\text{-}1)$$

We shall henceforth write η_λ for $\eta_\lambda(\mathcal{H}\sigma)$, $\tilde{\eta}_\lambda$ for $\eta_\lambda(\tilde{\mathcal{H}}\sigma)$, and $\tilde{\eta}_\lambda'$ for $\eta_\lambda'(\tilde{\mathcal{H}}\sigma)$. We also note that

$$\frac{h_{\tilde{\lambda}}'(\tilde{\mathcal{H}}\sigma)}{h_{\tilde{\lambda}}(\tilde{\mathcal{H}}\sigma)} = \frac{1}{2h_{\tilde{\lambda}}^2(\tilde{\mathcal{H}}\sigma)}\frac{d}{d(\tilde{\mathcal{H}}\sigma)}h_{\tilde{\lambda}}^2(\tilde{\mathcal{H}}\sigma)$$

$$= -\frac{1}{\tilde{\mathcal{H}}\sigma} - \frac{\tilde{\eta}_{\tilde{\lambda}}''}{2\tilde{\eta}_{\tilde{\lambda}}'} - i\,\tilde{\eta}_{\tilde{\lambda}}' . \qquad (4.2\text{-}2)$$

We now insert this expression for $h_{\tilde{\lambda}}'(\tilde{\mathcal{H}}\sigma)/h_{\tilde{\lambda}}(\tilde{\mathcal{H}}\sigma)$ into the expression for $\mathcal{I}_{\ell\ell,C}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$, Eq. 3.3-26. The result of inserting the term $-1/\tilde{\mathcal{H}}\sigma$ into this expression we denote by $\mathcal{I}_{\ell\ell,C,}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$. After carrying out the summations over $\tilde{\ell}^a$, $\tilde{\ell}^b$, and $\tilde{\lambda}$ we obtain

$$I_{\ell\ell,c_1}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = -\frac{2i}{8\mathcal{H}^3\sigma}$$

$$\times\,\delta_{\ell^a\bar{\ell}^a}\delta_{\ell^b\bar{\ell}^b}\sum_{\lambda\lambda'}(2\lambda+1)(2\lambda'+1)\left(S_{J00}^{\lambda\lambda'}\right)^2$$

$$\times\left[\frac{1}{h_{\lambda'}^2(\mathcal{H}\sigma)}\;\frac{j_\lambda(\mathcal{H}\sigma)}{h_\lambda^*(\mathcal{H}\sigma)} - \frac{1}{h_{\lambda'}^{*2}(\mathcal{H}\sigma)}\;\frac{j_\lambda(\mathcal{H}\sigma)}{h_\lambda(\mathcal{H}\sigma)}\right].$$

(4.2-3)

We now insert the remaining two terms in Eq. 4.2-2 into Eq. 3.3-26, and we denote the result by $I_{\ell\ell,c_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$. Thus

$$I_{\ell\ell,c_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2 = \delta_{\ell^a\bar{\ell}^a}\delta_{\ell^b\bar{\ell}^b}\frac{\sigma^2}{3\mathcal{H}}$$

$$\times(2J+1)\sum_{\lambda\tilde{\lambda}\tilde{\ell}^a\tilde{\ell}^b}\Big\{\tilde{\mathcal{H}}\Big[\left(S_{\tilde{\ell}^a00}^{1\ell^a}\right)^2\delta_{\ell^b\tilde{\ell}^b}+\left(S_{\tilde{\ell}^b00}^{1\ell^b}\right)^2\delta_{\ell^a\tilde{\ell}^a}\Big]$$

$$\times(2\lambda+1)\left(S_{\tilde{\lambda}00}^{1\lambda}\right)^2\eta_\lambda'\Big[\frac{\tilde{\eta}_{\tilde{\lambda}}''}{2\tilde{\eta}_{\tilde{\lambda}}'}\sin 2\eta_\lambda - 2\tilde{\eta}_{\tilde{\lambda}}'\sin^2\eta_\lambda\Big]\Big\}$$

$$
- \delta_{\ell^a \tilde{\ell}^a} \delta_{\ell^b \tilde{\ell}^b} \frac{\sigma^2}{3\mathcal{H}} (2J+1) \sum_{\substack{\lambda\lambda'\tilde{\lambda} \\ \tilde{\ell}^a \tilde{\ell}^b}} \Big\{ \tilde{\mathcal{H}} \Big[\big(S^{1\ell^a}_{\tilde{\ell}^a 00} \big)^2 \delta_{\ell^b \tilde{\ell}^b}
$$

$$
+ \big(S^{1\ell^b}_{\tilde{\ell}^b 00} \big)^2 \delta_{\ell^a \tilde{\ell}^a} \Big] (2\lambda+1) \big(S^{\lambda J}_{\lambda' 00} \big)^2 \big(S^{1\lambda}_{\tilde{\lambda} 00} \big)^2 \eta'_\lambda
$$

$$
\times \left[\frac{\tilde{\eta}''_{\tilde{\lambda}}}{2\tilde{\eta}'_{\tilde{\lambda}}} \sin 2(\eta_\lambda - \eta_{\lambda'}) - 2\tilde{\eta}'_{\tilde{\lambda}} \sin^2(\eta_\lambda - \eta_{\lambda'}) \right] \Big\} .
$$

(4.2-4)

It then follows that

$$
Q^{(1)}_{el, C_2}(\tilde{\ell}^a \tilde{\ell}^b \ell^a \ell^b)_2 = \delta_{\ell^a \tilde{\ell}^a} \delta_{\ell^b \tilde{\ell}^b} \frac{2\pi}{3} \frac{\sigma^2}{\mathcal{H}}
$$

$$
\times \sum_{\substack{\lambda\lambda'\tilde{\lambda} \\ \tilde{\ell}^a \tilde{\ell}^b}} \Big\{ \tilde{\mathcal{H}} \Big[\big(S^{1\ell^a}_{\tilde{\ell}^a 00} \big)^2 \delta_{\ell^b \tilde{\ell}^b} + \big(S^{1\ell^b}_{\tilde{\ell}^b 00} \big)^2 \delta_{\ell^a \tilde{\ell}^a} \Big]
$$

$$
\times (2\lambda+1) \big(S^{1\lambda}_{\tilde{\lambda} 00} \big)^2 \big(S^{\lambda 1}_{\lambda' 00} \big)^2 \eta'_\lambda
$$

$$
\times \left[\frac{\tilde{\eta}''_{\tilde{\lambda}}}{\tilde{\eta}'_{\tilde{\lambda}}} \sin 2(\eta_\lambda - \eta_{\lambda'}) - 4\tilde{\eta}'_{\tilde{\lambda}} \sin^2(\eta_\lambda - \eta_{\lambda'}) \right] \Big\} ,
$$

(4.2-5)

and

$$Q^{(2)}_{\ell\ell,C_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2 = \delta_{\ell^a\bar{\ell}^a}\delta_{\ell^b\bar{\ell}^b}\frac{4\pi}{9}\frac{\sigma^2}{\mathcal{H}}$$

$$\times \sum_{\substack{\lambda\lambda'\tilde{\lambda}\\ \tilde{\ell}^a\tilde{\ell}^b}} \Big\{ \tilde{\mathcal{H}} \Big[(S^{1\ell^a}_{\tilde{\ell}^a 00})^2 \delta_{\ell^b\tilde{\ell}^b} + (S^{1\ell^b}_{\tilde{\ell}^b 00})^2 \delta_{\ell^a\tilde{\ell}^a} \Big]$$

$$\times (2\lambda+1)\ (S^{1\lambda}_{\tilde{\lambda}00})^2 (S^{\lambda 2}_{\lambda' 00})^2 \eta'_\lambda$$

$$\times \Big[\frac{\tilde{\eta}''_{\tilde{\lambda}}}{\tilde{\eta}'_{\tilde{\lambda}}} \sin 2(\eta_\lambda - \eta_{\lambda'}) - 4\,\tilde{\eta}'_{\tilde{\lambda}} \sin^2(\eta_\lambda - \eta_{\lambda'}) \Big] \Big\} \qquad (4.2\text{-}6)$$

Consider now an expression of the form

$$X = \sum_{\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b} f(\bar{\ell}^a\bar{\ell}^b)\, Q^{(1)}_{\ell\ell,C_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2 . \qquad (4.2\text{-}7)$$

The quantity $Q^{(1)}_{\ell\ell,C_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2$ may be written in the general form

$$Q^{(1)}_{\ell\ell,C_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2 = \delta_{\ell^a\bar{\ell}^a}\delta_{\ell^b\bar{\ell}^b}\sum_{\tilde{\ell}^a\tilde{\ell}^b} q^{(1)}_{\ell\ell,C_2}(\ell^a\ell^b\tilde{\ell}^a\tilde{\ell}^b)_2 . \qquad (4.2\text{-}8)$$

Then

$$X = \sum_{\bar{\ell}^a \bar{\ell}^b \tilde{\ell}^a \tilde{\ell}^b} f(\bar{\ell}^a \bar{\ell}^b)\, g^{(1)}_{\ell\ell, C_2} (\bar{\ell}^a \bar{\ell}^b \tilde{\ell}^a \tilde{\ell}^b)_2$$

$$= \sum_{\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b} f(\bar{\ell}^a \bar{\ell}^b)\, g^{(1)}_{\ell\ell, C_2} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2 \, . \qquad (4.2\text{-}9)$$

Hence in an expression of this kind we may use $g^{(1)}_{\ell\ell, C_2} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2$ in place of $Q^{(1)}_{\ell\ell, C_2} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2$. We now define $g^{(1)} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)$ by the equation

$$g^{(1)} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b) = Q^{(1)} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_0$$

$$+ \left(\frac{\delta}{\sigma}\right)^2 \Big[Q^{(1)}_{\ell\ell, A+B+C_1} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2 + g^{(1)}_{\ell\ell, C_2} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2$$

$$+ Q^{(1)}_{inel} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2 \Big] + \cdots \, . \qquad (4.2\text{-}10)$$

We note that $g^{(1)} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)$ is identical with $Q^{(1)} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)$, except that $Q^{(1)}_{\ell\ell, C_2} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2$ has been replaced by $g^{(1)}_{\ell\ell, C_2} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2$; we define $g^{(2)} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)$ in an identical fashion. In Chapter VI we shall see that the expressions for the quantum mechanical transport coefficients into which $\mathcal{Q}^{(1)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$ and $\mathcal{Q}^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$ are to be inserted are of the form of the quantity X given in Eq. 4.2-7. Therefore, we shall henceforth work with $q^{(1)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$ and $q^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$, instead of $\mathcal{Q}^{(1)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$ and $\mathcal{Q}^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$.

The summations over λ' and $\bar{\lambda}$ may be carried out in Eqs. 4.2-5 and 4.2-6 by using the explicit expressions for the Wigner coefficients given in Eqs. A.1-20 through A.1-24. The result is:

$$
\begin{aligned}
q^{(1)}_{\ell\ell,c_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2 = {} & \frac{2\pi}{3}\,\frac{\mathcal{H}}{\mathcal{H}}\,\sigma^2 \\
\times & \left\{ \left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2 \delta_{\ell^b\bar{\ell}^b} + \left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2 \delta_{\ell^a\bar{\ell}^a} \right\} \sum_{\lambda} \\
& \left\{ \frac{(\lambda+1)^2}{2\lambda+1}\, \bar{\eta}'_\lambda \left[\frac{\eta''_{\lambda+1}}{\eta'_{\lambda+1}} \sin 2(\bar{\eta}_\lambda - \bar{\eta}_{\lambda+1}) - 4\eta'_{\lambda+1} \sin^2(\bar{\eta}_\lambda - \bar{\eta}_{\lambda+1}) \right] \right. \\
& + \frac{\lambda(\lambda+1)}{2\lambda+1}\, \bar{\eta}'_\lambda \left[\frac{\eta''_{\lambda+1}}{\eta'_{\lambda+1}} \sin 2(\bar{\eta}_\lambda - \bar{\eta}_{\lambda-1}) - 4\eta'_{\lambda+1} \sin^2(\bar{\eta}_\lambda - \bar{\eta}_{\lambda-1}) \right] \\
& + \frac{\lambda(\lambda+1)}{2\lambda+1}\, \bar{\eta}'_\lambda \left[\frac{\eta''_{\lambda-1}}{\eta'_{\lambda-1}} \sin 2(\bar{\eta}_\lambda - \bar{\eta}_{\lambda+1}) - 4\eta'_{\lambda-1} \sin^2(\bar{\eta}_\lambda - \bar{\eta}_{\lambda+1}) \right] \\
& \left. + \frac{\lambda^2}{2\lambda+1}\, \bar{\eta}'_\lambda \left[\frac{\eta''_{\lambda-1}}{\eta'_{\lambda-1}} \sin 2(\bar{\eta}_\lambda - \bar{\eta}_{\lambda-1}) - 4\eta'_{\lambda-1} \sin^2(\bar{\eta}_\lambda - \bar{\eta}_{\lambda-1}) \right] \right\}.
\end{aligned}
\tag{4.2-11}
$$

and

$$\mathcal{g}^{(2)}_{\mathcal{e},C_2}(\bar{e}^a\bar{e}^b e^a e^b)_2 = \frac{2\pi}{3}\frac{\mathcal{H}}{\bar{\mathcal{H}}}\sigma^2$$

$$\times\left\{(S^{1\bar{e}^a}_{e^a 00})^2\delta_{e^b\bar{e}^b} + (S^{1\bar{e}^b}_{e^b 00})^2\delta_{e^a\bar{e}^a}\right\}\sum_\lambda$$

$$\left\{\frac{(\lambda-1)\lambda^2}{(2\lambda-1)(2\lambda+1)}\bar{\eta}_\lambda'\left[\frac{\eta''_{\lambda-1}}{\eta'_{\lambda-1}}\sin 2(\bar{\eta}_\lambda-\bar{\eta}_{\lambda-2}) - 4\eta'_{\lambda-1}\sin^2(\bar{\eta}_\lambda-\bar{\eta}_{\lambda-2})\right]\right.$$

$$+\frac{\lambda(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)}\bar{\eta}_\lambda'\left[\frac{\eta''_{\lambda-1}}{\eta'_{\lambda-1}}\sin 2(\bar{\eta}_\lambda-\bar{\eta}_{\lambda+2}) - 4\eta'_{\lambda-1}\sin^2(\bar{\eta}_\lambda-\bar{\eta}_{\lambda+2})\right]$$

$$+\frac{(\lambda-1)\lambda(\lambda+1)}{(2\lambda-1)(2\lambda+1)}\bar{\eta}_\lambda'\left[\frac{\eta''_{\lambda+1}}{\eta'_{\lambda+1}}\sin 2(\bar{\eta}_\lambda-\bar{\eta}_{\lambda-2}) - 4\eta'_{\lambda+1}\sin^2(\bar{\eta}_\lambda-\bar{\eta}_{\lambda-2})\right]$$

$$\left.+\frac{(\lambda+1)^2(\lambda+2)}{(2\lambda+1)(2\lambda+3)}\bar{\eta}_\lambda'\left[\frac{\eta''_{\lambda+1}}{\eta'_{\lambda+1}}\sin 2(\bar{\eta}_\lambda-\bar{\eta}_{\lambda+2}) - 4\eta'_{\lambda+1}\sin^2(\bar{\eta}_\lambda-\bar{\eta}_{\lambda+2})\right]\right\}. \tag{4.2-12}$$

We have now completely expressed the contribution to $\mathcal{g}^{(1)}$ and $\mathcal{g}^{(2)}$ arising from the second and third terms in Eq. 4.2-2 in terms of rigid sphere phase shifts and their derivatives.

We must now find the contributions to $\mathcal{g}^{(1)}$ and $\mathcal{g}^{(2)}$ arising from $I_{\mathcal{e},A+B}(\bar{e}^a\bar{e}^b e^a e^b|J)_2$, Eq. 3.3-23 and $I_{\mathcal{e},C_1}(\bar{e}^a\bar{e}^b e^a e^b|J)_2$, Eq. 4.2-3. These quantities are of the same form and may therefore be combined. When the

$\mathcal{Q}$'s arising from the sum are evaluated we find that

$$\mathcal{Q}^{(1)}_{\ell\ell, A+B+C,}\ (\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_2$$

$$= -\frac{8\pi}{3}\frac{\sigma}{\mathcal{H}}\,\delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}\sum_{\lambda}(\lambda+1)(\eta'_{\lambda+1}-\eta'_{\lambda})\sin 2(\eta_{\lambda+1}-\eta_{\lambda}), \tag{4.2-13}$$

and

$$\mathcal{Q}^{(2)}_{\ell\ell, A+B+C,}\ (\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_2$$

$$= -\frac{8\pi}{3}\frac{\sigma}{\mathcal{H}}\,\delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}\sum_{\lambda}\frac{(\lambda+1)(\lambda+2)}{(2\lambda+3)}(\eta'_{\lambda+2}-\eta'_{\lambda})\sin 2(\eta_{\lambda+2}-\eta_{\lambda}). \tag{4.2-14}$$

This completes the evaluation of the elastic contributions to $g^{(1)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})$ and $g^{(2)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})$.

Section 4.3 <u>The Evaluation of $\mathcal{Q}^{(1)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_2$ and $\mathcal{Q}^{(2)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_2$</u> -- The Inelastic Part

The expression for $I_{inel}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b}|J)_2$ is given by Eq. 3.4-4. For any given value of J the sum may be reduced to a single sum over λ, since λ', $\bar{\lambda}$, and $\bar{\lambda}'$ are restricted to a finite number of values by the Wigner coefficients. When this is done, and explicit expressions for the Wigner and Racah coefficients are inserted into the equation, (see Appendix III) we obtain the following results:

$$I_{inel}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | 0)_2 = \frac{1}{3} \frac{\mathcal{H}}{\bar{\mathcal{H}}} \sigma^2$$

$$\times \left\{ \left(S_{\ell^a 00}^{1\bar{\ell}^a} \right)^2 \delta_{\ell^b \bar{\ell}^b} + \left(S_{\ell^b 00}^{1\bar{\ell}^b} \right)^2 \delta_{\ell^a \bar{\ell}^a} \right\}$$

$$\times \sum_\lambda (\lambda+1)\left(\bar{\eta}_\lambda' \eta_{\lambda+1}' + \eta_\lambda' \bar{\eta}_{\lambda+1}' \right) \quad , \qquad (4.3\text{-}1)$$

$$I_{inel}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | 1)_2 = \frac{2\mathcal{H}}{\bar{\mathcal{H}}} \sigma^2$$

$$\times \left\{ \left(S_{\ell^a 00}^{1\bar{\ell}^a} \right)^2 \delta_{\ell^b \bar{\ell}^b} + \left(S_{\ell^b 00}^{1\bar{\ell}^b} \right)^2 \delta_{\ell^a \bar{\ell}^a} \right\} \sum_\lambda$$

$$\Bigg[\frac{(\lambda+1)(\lambda+2)}{(2\lambda+3)} \sqrt{\eta_\lambda' \bar{\eta}_{\lambda+1}' \eta_{\lambda+1}' \bar{\eta}_{\lambda+2}'} \cos(\bar{\eta}_{\lambda+2} - \bar{\eta}_{\lambda+1} + \eta_{\lambda+1} - \eta_\lambda)$$

$$+ \frac{(\lambda+1)(\lambda+2)}{(2\lambda+3)} \sqrt{\bar{\eta}_\lambda' \bar{\eta}_{\lambda+1}' \eta_{\lambda+1}' \eta_{\lambda+2}'} \cos(\eta_{\lambda+2} - \eta_{\lambda+1} + \bar{\eta}_{\lambda+1} - \bar{\eta}_\lambda)$$

$$- \frac{(\lambda+1)}{(2\lambda+1)(2\lambda+3)} \sqrt{\bar{\eta}_\lambda' \eta_\lambda' \bar{\eta}_{\lambda+1}' \eta_{\lambda+1}'} \cos(\eta_\lambda - \bar{\eta}_\lambda + \bar{\eta}_{\lambda+1} - \eta_{\lambda+1}) \Bigg] .$$

$$(4.3\text{-}2)$$

$$Q^{(1)}_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2 = \frac{4\pi}{3}\,\frac{\mathcal{H}}{\bar{\mathcal{H}}}\,\sigma^2\Big\{\big(S^{1\bar{\ell}^a}_{\ell^a00}\big)^2\delta_{\ell^b\bar{\ell}^b}$$

$$+\big(S^{1\bar{\ell}^b}_{\ell^b00}\big)^2\delta_{\ell^a\bar{\ell}^a}\Big\}\sum_{\lambda}\Big\{(\lambda+1)(\bar{\eta}'_\lambda\,\eta'_{\lambda+1}+\eta'_\lambda\,\bar{\eta}'_{\lambda+1})$$

$$+\frac{2(\lambda+1)}{(2\lambda+1)(2\lambda+3)}\sqrt{\eta'_\lambda\,\bar{\eta}'_\lambda\,\eta'_{\lambda+1}\,\bar{\eta}'_{\lambda+1}}\cos(\eta_\lambda-\bar{\eta}_\lambda+\bar{\eta}_{\lambda+1}-\eta_{\lambda+1})$$

$$-\frac{2(\lambda+1)(\lambda+2)}{(2\lambda+3)}\Big[\sqrt{\eta'_\lambda\,\eta'_{\lambda+1}\,\bar{\eta}'_{\lambda+1}\,\bar{\eta}'_{\lambda+2}}\cos(\bar{\eta}_{\lambda+2}-\bar{\eta}_{\lambda+1}+\eta_{\lambda+1}-\eta_\lambda)$$

$$+\sqrt{\bar{\eta}'_\lambda\,\bar{\eta}'_{\lambda+1}\,\eta'_{\lambda+1}\,\eta'_{\lambda+2}}\cos(\eta_{\lambda+2}-\eta_{\lambda+1}+\bar{\eta}_{\lambda+1}-\bar{\eta}_\lambda)\Big]\Big\}. \qquad (4.3\text{-}4)$$

and

$$I_{inel}(\bar{l}^a \bar{l}^b l^a l^b \,|\, 2)_2 = \frac{5}{3}\frac{\mathcal{H}}{\bar{\mathcal{H}}}\sigma^2 \left\{ \left(S^{1\bar{l}^a}_{l^a 00}\right)^2 \delta_{l^b \bar{l}^b} + \left(S^{1\bar{l}^b}_{l^b 00}\right)^2 \delta_{l^a \bar{l}^a} \right\}$$

$$\sum_\lambda \left\{ \frac{3\lambda(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)} \left[\sqrt{\eta'_{\lambda-1}\bar{\eta}'_\lambda \eta'_{\lambda+1}\bar{\eta}'_{\lambda+2}} \cos(\bar{\eta}_{\lambda+2} - \bar{\eta}_\lambda + \eta_{\lambda+1} - \eta_{\lambda-1}) \right.\right.$$

$$\left. + \sqrt{\bar{\eta}'_{\lambda-1}\eta'_\lambda \bar{\eta}'_{\lambda+1}\eta'_{\lambda+2}} \cos(\eta_{\lambda+2} - \eta_\lambda + \bar{\eta}_{\lambda+1} - \bar{\eta}_{\lambda-1}) \right]$$

$$- \frac{6(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)(2\lambda+5)} \left[\sqrt{\bar{\eta}'_\lambda \eta'_{\lambda+1}\eta'_{\lambda+1}\bar{\eta}'_{\lambda+2}} \cos(\bar{\eta}_{\lambda+2} - \bar{\eta}_\lambda) \right.$$

$$\left. + \sqrt{\eta'_\lambda \bar{\eta}'_{\lambda+1}\bar{\eta}'_{\lambda+1}\eta'_{\lambda+2}} \cos(\eta_{\lambda+2} - \eta_\lambda) \right]$$

$$\left. + \frac{\lambda(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)} \left[\bar{\eta}'_\lambda \eta'_{\lambda+1} + \eta'_\lambda \bar{\eta}'_{\lambda+1} \right] \right\}. \qquad (4.3\text{-}3)$$

These quantities may now be combined to form $Q^{(1)}_{inel}$ and $Q^{(2)}_{inel}$.

$$
\begin{aligned}
Q^{(2)}_{inel}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_{2} = {} & \frac{8\pi}{3}\frac{\mathcal{H}}{\bar{\mathcal{H}}}\sigma^{2}\left\{\left(S^{1\bar{\ell}^{a}}_{\ell^{a}00}\right)^{2}\delta_{\ell^{b}\bar{\ell}^{b}}+\left(S^{1\bar{\ell}^{b}}_{\ell^{b}00}\right)^{2}\delta_{\ell^{a}\bar{\ell}^{a}}\right\} \\
& \sum_{\lambda}\Bigg\{\frac{(\lambda+1)^{3}}{(2\lambda+1)(2\lambda+3)}\left(\bar{\eta}'_{\lambda}\eta'_{\lambda+1}+\eta'_{\lambda}\bar{\eta}'_{\lambda+1}\right) \\
& +\frac{2(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)(2\lambda+5)}\Big[\sqrt{\bar{\eta}'_{\lambda}\eta'_{\lambda+1}\eta'_{\lambda+1}\bar{\eta}'_{\lambda+2}}\cos(\bar{\eta}_{\lambda+2}-\bar{\eta}_{\lambda}) \\
& \qquad +\sqrt{\eta'_{\lambda}\bar{\eta}'_{\lambda+1}\bar{\eta}'_{\lambda+1}\eta'_{\lambda+2}}\cos(\eta_{\lambda+2}-\eta_{\lambda})\Big] \\
& -\frac{\lambda(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)}\Big[\sqrt{\eta'_{\lambda-1}\bar{\eta}'_{\lambda}\eta'_{\lambda+1}\bar{\eta}'_{\lambda+2}}\cos(\bar{\eta}_{\lambda+2}-\bar{\eta}_{\lambda}+\eta_{\lambda+1}-\eta_{\lambda-1}) \\
& \qquad +\sqrt{\bar{\eta}'_{\lambda-1}\eta'_{\lambda}\bar{\eta}'_{\lambda+1}\eta'_{\lambda+2}}\cos(\eta_{\lambda+2}-\eta_{\lambda}+\bar{\eta}_{\lambda+1}-\bar{\eta}_{\lambda-1})\Big]\Bigg\}.
\end{aligned}
\tag{4.3-5}
$$

We have now obtained expressions for all the quantities which are necessary for an exact quantum mechanical evaluation of the transport coefficients for a gas of loaded spheres. The formulas for these coefficients are given in Chapter VI. For the evaluation of the relaxation time, only the total inelastic cross section, $I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|0)_2$, given by Eq. 4.3-1, is needed. For the calculation of the shear viscosity the quantities $\mathcal{Q}^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$ and $I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|2)_2$, Eq. 4.3-3, are needed. The zero order term in the expansion of $\mathcal{Q}^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$ in powers of δ/σ, $\mathcal{Q}^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_0$, is given by Eq. 4.1-20; the second non-vanishing term, $\mathcal{Q}^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2$ which is the coefficient of $(\delta/\sigma)^2$ in that expansion, consists of the sum of the quantities given by Eqs. 4.2-12, 4.2-14, and 4.3-5.

For the evaluation of the coefficient of thermal conductivity $\mathcal{Q}^{(1)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$ is needed, along with $I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|1)_2$, Eq. 4.3-2. The term corresponding to rigid spheres, $\mathcal{Q}^{(1)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_0$, is given by Eq. 4.1-19, and $\mathcal{Q}^{(1)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2$ is equal to the sum of the quantities given by Eqs. 4.2-11, 4.2-13, and 4.3-4.

In order to obtain numerical values for the transport coefficients, the phase shifts appearing in these expressions for the moments of the cross section would have to be computed from the definition of the phase shift in terms of Bessel functions, Eq. 4.1-9, and the summations over λ carried out numerically. These moments would be inserted into the appropriate expressions in Chapter VI, and the integrations over the incoming kinetic energy and the sums over the incoming and outgoing internal states carried out.

In this thesis, however, we do not evaluate the quantum mechanical results numerically, but instead we obtain the classical limit of the transport coefficients. In the following chapter we shall expand the quantities given in this chapter in power series in Planck's constant. Then, in Chapter VI, we shall evaluate the transport coefficients in the limit that Planck's constant approaches zero.

CHAPTER V

EXPANSIONS OF THE CROSS SECTION MOMENTS IN POWERS OF PLANCK'S CONSTANT

In this chapter we derive expansions of the cross section moments obtained in Chapter IV in asymptotic power series in Planck's constant. These are developed by use of asymptotic series developments of the Bessel functions which occur in the definition of the spherical phase shift.

Section 5.1 The Expansion of the Phase Shift

We begin by defining certain quantities which will be used throughout the discussion in this chapter:

$$k = \frac{\hbar}{\sqrt{2\mu}} , \tag{5.1-1}$$

where $\hbar$ is Planck's constant and μ is the reduced mass of the pair of colliding molecules;

$$L = (\lambda + \tfrac{1}{2})\, k \quad ; \tag{5.1-2}$$

the kinetic energy of relative motion,

$$E = k^2 \mathcal{H}^2 \quad ; \tag{5.1-3}$$

the impact parameter,

$$b = \frac{L}{\sqrt{E}} \quad ; \tag{5.1-4}$$

the dimensionless relative velocity,

$$\gamma = \sqrt{\frac{E}{kT}} \quad ; \tag{5.1-5}$$

$\epsilon_{\bar{\ell}^a}$ = (internal energy of state with quantum number $\bar{\ell}^a$) /kT;

(5.1-6)

$$\Delta E = E - \bar{E} \quad ; \tag{5.1-7}$$

and

$$\Delta\epsilon(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b) = \epsilon_{\ell^a} + \epsilon_{\ell^b} - \epsilon_{\bar{\ell}^a} - \epsilon_{\bar{\ell}^b} . \tag{5.1-8}$$

Conservation of energy requires that

$$\frac{\bar{E}}{kT} + \epsilon_{\bar{\ell}^a} + \epsilon_{\bar{\ell}^b} = \frac{E}{kT} + \epsilon_{\ell^a} + \epsilon_{\ell^b} , \tag{5.1-9}$$

or,

$$\gamma^2 = \bar{\gamma}^2 - \Delta\epsilon(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b) . \tag{5.1-10}$$

We have thus far considered the phase shift $\eta_\lambda(\varkappa\sigma)$ as a function of λ and $\varkappa\sigma$. We now consider it a function of the three independent variables L, E, and $\hbar$ and write

$$\eta(L, E, \hbar) = \eta_\lambda(\varkappa\sigma). \tag{5.1-11}$$

Then

$$\left(\frac{\partial\eta}{\partial E}\right)_{L,\hbar} = \left(\frac{\partial\lambda}{\partial E}\right)_{L,\hbar}\left(\frac{\partial\eta_\lambda}{\partial\lambda}\right)_{\varkappa\sigma} + \left(\frac{\partial(\varkappa\sigma)}{\partial E}\right)_{L,\hbar}\left(\frac{\partial\eta_\lambda}{\partial(\varkappa\sigma)}\right)_\lambda$$

$$= \frac{\sigma}{2\sqrt{E}\,\hbar}\,\eta_\lambda'(\varkappa\sigma), \tag{5.1-12}$$

and

$$\eta_\lambda'(\varkappa\sigma) = \frac{2\sqrt{E}\,\hbar}{\sigma}\,\frac{\partial\eta}{\partial E}(L, E, \hbar). \tag{5.1-13}$$

The defining equation for $\eta_\lambda(\varkappa\sigma)$, Eq. 4.1-9, may be written in terms of ordinary Bessel functions of half odd integral order as

$$\eta_\lambda(\varkappa\sigma) = \tan^{-1}\left[(-1)^{\lambda+1}\,\frac{J_{\lambda+\frac{1}{2}}(\varkappa\sigma)}{J_{-\lambda-\frac{1}{2}}(\varkappa\sigma)}\right]. \tag{5.1-14}$$

But

$$J_{-\lambda-\frac{1}{2}}(\varkappa\sigma) = -\sin\left[(\lambda+\tfrac{1}{2})\pi\right] N_{\lambda+\frac{1}{2}}(\varkappa\sigma)$$

$$= (-1)^{\lambda+1} N_{\lambda+\frac{1}{2}}(\varkappa\sigma), \qquad (5.1\text{-}15)$$

where N is the Bessel function of the second kind. Watson[34] uses the symbol Y for this function. The asymptotic expansion of $\eta(L,E,\hbar)$ in powers of $\hbar$ is based on the asymptotic expansion formulas for the Bessel functions given by Watson. When the order of the function is less than the argument we have

$$J_\nu(\nu\sec\beta) \sim \sqrt{\frac{2}{\nu\pi\tan\beta}}\Bigg[\cos(\nu\tan\beta-\nu\beta-\tfrac{1}{4}\pi)$$

$$\times\sum_{m=0}^{\infty}\frac{(-1)^m\,\Gamma(2m+\frac{1}{2})}{\Gamma(\frac{1}{2})}\,\frac{A_{2m}}{(\frac{1}{2}\nu\tan\beta)^{2m}}$$

$$+\sin(\nu\tan\beta-\nu\beta-\tfrac{1}{4}\pi)$$

$$\times\sum_{m=0}^{\infty}\frac{(-1)^m\,\Gamma(2m+\frac{3}{2})}{\Gamma(\frac{1}{2})}\,\frac{A_{2m+1}}{(\frac{1}{2}\nu\tan\beta)^{2m+1}}\Bigg], \qquad (5.1\text{-}16)$$

and

$$N_\nu(\nu \sec\beta) \sim \sqrt{\frac{2}{\nu\pi\tan\beta}} \Big[\sin(\nu\tan\beta - \nu\beta - \tfrac{1}{4}\pi)$$

$$\times \sum_{m=0}^{\infty} (-1)^m \frac{\Gamma(2m+\frac{1}{2})}{\Gamma(\frac{1}{2})} \frac{A_{2m}}{(\frac{1}{2}\nu\tan\beta)^{2m}}$$

$$- \cos(\nu\tan\beta - \nu\beta - \tfrac{1}{4}\pi)$$

$$\times \sum_{m=0}^{\infty} \frac{(-1)^m \Gamma(2m+\frac{3}{2})}{\Gamma(\frac{1}{2})} \frac{A_{2m+1}}{(\frac{1}{2}\nu\tan\beta)^{2m+1}} \Big] . \qquad (5.1\text{-}17)$$

In these equations β is a fixed positive acute angle and the A_k are functions of β ; in particular, $A_0 = 1$. If we now set $\nu = \lambda + \frac{1}{2} = L/\hbar$ and $\sec\beta = \sigma\sqrt{E}/L$ we find that

$$\eta(L,E,\hbar) \sim \frac{1}{\hbar}\eta^{(0)}(L,E) + \eta^{(1)}(L,E) + \cdots , \qquad (5.1\text{-}18)$$

where

$$\eta^{(0)}(L,E) = L\cos^{-1}\left(\frac{L}{\sigma\sqrt{E}}\right) - \sqrt{\sigma^2 E - L^2} \;,\; 0 < \frac{L}{\sigma\sqrt{E}} < 1 . \qquad (5.1\text{-}19)$$

Explicit expressions for $\eta^{(j)}(L,E)$ for $j > 0$ will not be needed in the present work.

In the case that the order of the function is greater than the argument we have

$$J_\nu(\nu \operatorname{sech} \alpha) \sim \frac{e^{\nu(\tanh\alpha - \alpha)}}{\sqrt{2\pi\nu\tanh\alpha}}$$

$$\times \sum_{m=0}^{\infty} \frac{\Gamma(m+\frac{1}{2})}{\Gamma(\frac{1}{2})} \frac{A_m}{(\frac{1}{2}\nu\tanh\alpha)^m} , \tag{5.1-20}$$

and

$$N_\nu(\nu \operatorname{sech} \alpha) \sim - \frac{e^{\nu(\alpha - \tanh\alpha)}}{\sqrt{\frac{1}{2}\pi\nu\tanh\alpha}}$$

$$\times \sum_{m=0}^{\infty} \frac{\Gamma(m+\frac{1}{2})}{\Gamma(\frac{1}{2})} \frac{(-1)^m A_m}{(\frac{1}{2}\nu\tanh\alpha)^m} . \tag{5.1-21}$$

Since ν is equal to $L/\hbar$ and $\tanh\alpha - \alpha < 0$ for α real, we find that

$$\lim_{\hbar\to 0} \left[\hbar^{-N} \frac{J_{\lambda+\frac{1}{2}}(\varkappa\sigma)}{N_{\lambda+\frac{1}{2}}(\varkappa\sigma)} \right] = 0 , N = 0, 1, 2, \cdots . \tag{5.1-22}$$

Hence we may take

$$\eta(L, E, \hbar) = 0, \quad \frac{L}{\sigma\sqrt{E}} > 1. \tag{5.1-23}$$

The following formulas, obtained by differentiating the expression for $\eta^{(0)}(L, E)$, Eq. 5.1-19, are used frequently in the following work:

$$\eta^{(0)\prime}(L,E) = -\hbar\sqrt{1-\frac{L^2}{\sigma^2 E}} = -\hbar\sqrt{1-\frac{b^2}{\sigma^2}}\,, \qquad (5.1\text{-}24)$$

$$\frac{\partial\eta^{(0)\prime}}{\partial L}(L,E) = \frac{\hbar L}{\sigma^2 E}\,\frac{1}{\sqrt{1-\frac{L^2}{\sigma^2 E}}} = \frac{\hbar}{\sigma^2 E}\,\frac{b}{\sqrt{1-\frac{b^2}{\sigma^2}}}\,, \qquad (5.1\text{-}25)$$

and

$$\frac{\partial\eta^{(0)\prime}}{\partial E}(L,E) = -\frac{\hbar L^2}{2\sigma^2 E^2}\,\frac{1}{\sqrt{1-\frac{L^2}{\sigma^2 E}}} = -\frac{\hbar}{2\sigma^2 E}\,\frac{b^2}{\sqrt{1-\frac{b^2}{\sigma^2}}}\,. \qquad (5.1\text{-}26)$$

These formulas hold for $b < \sigma$. For $b > \sigma$ the three functions are taken to be zero.

We illustrate the use of these formulas by computing the zero order term in the expansion of $\mathcal{Q}^{(1)}(\bar{l}^a\bar{l}^b l^a l^b)_0$, Eq. 4.1-19, in powers of $\hbar$. In order to carry out the sum over λ, we make use of the Euler-Maclaurin[35] series. This series furnishes a method for changing discrete sums to integrals. It states that

$$\sum_{\lambda=0}^{\infty} f(\lambda) = \int_0^{\infty} f(\lambda)\, d\lambda + \frac{1}{2} f(0)$$

$$+ \frac{1}{2} f(\infty) + \sum_{r=1,3,5,\ldots} \frac{\mathcal{B}_{r+1}}{(r+1)!} \frac{\partial^r f}{\partial \lambda^r}\Bigg]_0^{\infty} , \qquad (5.1\text{-}27)$$

where the $\mathcal{B}_K$ are real numbers known as the Bernoulli numbers. When we apply this formula to our expression for $Q^{(1)}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_0$, Eq. 4.1-19, and change variables from λ and $\mathcal{H}$ to L and E we obtain

$$Q^{(1)}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_0 = \delta_{\ell^a \bar{\ell}^a}\, \delta_{\ell^b \bar{\ell}^b}\, \frac{4\pi}{E}$$

$$\times \Bigg\{ \int_{\frac{1}{2}\hbar}^{\infty} (L + \tfrac{1}{2}\hbar) \sin^2 \left[\eta(L+\hbar, E, \hbar) - \eta(L, E, \hbar) \right] dL$$

$$+ \hbar^2 \sin^2 \left[\eta(\tfrac{3}{2}\hbar, E, \hbar) - \eta(\tfrac{1}{2}\hbar, E, \hbar) \right]$$

$$+ \lim_{L \to \infty} \hbar (L + \tfrac{1}{2}\hbar) \sin^2 \left[\eta(L+\hbar, E, \hbar) - \eta(L, E, \hbar) \right]$$

$$+ \sum_{r=1,3,5,\ldots} \frac{\mathcal{B}_{r+1}}{(r+1)!} \hbar^{r+1} \frac{\partial^r}{\partial L^r} \Big[(L + \tfrac{1}{2}\hbar) \sin^2 \left[\eta(L+\hbar, E, \hbar) - \eta(L, E, \hbar) \right] \Big]_{\frac{1}{2}\hbar}^{\infty} \Bigg\} .$$

(5.1-28)

The only term in this expression which is of zero order in $\hbar$ is the integral. The other terms are of at least first order in $\hbar$, and those evaluated at infinity vanish by Eq. 5.1-23.

Let us now consider the integral on the right hand side in Eq. 5.1-28. To lowest order we may neglect the $\frac{1}{2}\hbar$ in comparison with the L , and we may change the lower limit of integration from $\frac{1}{2}\hbar$ to 0 . Also to lowest order in $\hbar$ we may write

$$\begin{aligned} \eta(L+\hbar,E,\hbar)-\eta(L,E,\hbar) &= \frac{\partial\eta^{(0)}}{\partial L} = \cos^{-1}\left(\frac{L}{\sigma\sqrt{E}}\right), & \frac{L}{\sqrt{E}} &< \sigma; \\ &= 0\ , & \frac{L}{\sqrt{E}} &> \sigma. \end{aligned} \tag{5.1-29}$$

Finally, changing the integration over L to an integration over b we have

$$\begin{aligned} Q^{(1)}(\bar{\ell}^{\circ}\bar{\ell}^{b}\ell^{\circ}\ell^{b})_0 &= \delta_{\ell^{\circ}\bar{\ell}^{a}}\delta_{\ell^{b}\bar{\ell}^{b}}\, 4\pi\int_0^{\sigma} b\left(1-\frac{b^2}{\sigma^2}\right)db + O(\hbar) \\ &= \pi\sigma^2\,\delta_{\ell^{\circ}\bar{\ell}^{a}}\,\delta_{\ell^{b}\bar{\ell}^{b}} + O(\hbar). \end{aligned} \tag{5.1-30}$$

In the same manner one can show that

$$Q^{(2)}(\bar{\ell}^{\circ}\bar{\ell}^{b}\ell^{\circ}\ell^{b})_0 = \frac{2\pi}{3}\sigma^2\,\delta_{\ell^{\circ}\bar{\ell}^{a}}\,\delta_{\ell^{b}\bar{\ell}^{b}} + O(\hbar). \tag{5.1-31}$$

As $\hbar$ approaches zero, these quantities approach the known classical values[36].

Section 5.2 The Expansion of $I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$, in Powers of $\hbar$

The formula for $I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|0)_2$ is given by Eq. 4.3-1. In order to determine how many and which terms are to be retained in the expansion of this quantity let us consider a quantity

$$\mathcal{J} = \sum_{\ell^a\ell^b\bar{\ell}^a\bar{\ell}^b} \Delta\epsilon(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b) I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|0)_2 . \quad (5.2\text{-}1)$$

We wish to find the lowest order term in the expansion of $\mathcal{J}$ in powers of $\hbar$. First we note from Eq. 1.2-3, which gives the energy corresponding to the quantum number ℓ , that

$$\Delta\epsilon(\bar{\ell}^a\bar{\ell}^b\ \bar{\ell}^a+1\ \bar{\ell}^b) = \frac{\hbar^2}{2IkT}\Big[(\bar{\ell}^a+1)(\bar{\ell}^a+2)$$

$$-\bar{\ell}^a(\bar{\ell}^a+1)\Big] = \frac{\hbar^2}{IkT}(\bar{\ell}^a+1), \quad (5.2\text{-}2)$$

and that

$$\Delta\epsilon(\bar{\ell}^a\bar{\ell}^b\ \bar{\ell}^a-1\ \bar{\ell}^b) = \frac{\hbar^2}{2IkT}\Big[(\bar{\ell}^a-1)\bar{\ell}^a$$

$$-\bar{\ell}^a(\bar{\ell}^a+1)\Big] = -\frac{\hbar^2}{IkT}\bar{\ell}^a, \quad (5.2\text{-}3)$$

with similar formulas for $\Delta\ell^b = \pm 1$. We note that these are the only transitions which need be considered, since the quantity

$$\left\{\left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2 \delta_{\ell^b \bar{\ell}^b} + \left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2 \delta_{\ell^a \bar{\ell}^a}\right\} \tag{5.2-4}$$

is zero except in these four cases.

Using the explicit expressions for $S^{1\bar{\ell}^a}_{\ell^a 00}$ given in Eqs. A.1-20 and A.1-21 we can carry out the following sums:

$$\sum_{\ell^a \ell^b} \Delta\epsilon(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b) \left\{\left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2 \delta_{\ell^b \bar{\ell}^b} + \left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2 \delta_{\ell^a \bar{\ell}^a}\right\}$$
$$= \frac{\hbar^2}{\Gamma kT} , \tag{5.2-5}$$

and

$$\sum_{\ell^a \ell^b} \left[\Delta\epsilon(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)\right]^2 \left\{\left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2 \delta_{\ell^b \bar{\ell}^b} + \left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2 \delta_{\ell^a \bar{\ell}^a}\right\}$$
$$= \left(\frac{\hbar^2}{2\Gamma kT}\right)^2 \left[\frac{(\bar{\ell}^a)^3}{2\bar{\ell}^a+1} + \frac{(\bar{\ell}^a+1)^3}{2\bar{\ell}^a+1} + \frac{(\bar{\ell}^b)^3}{2\bar{\ell}^b+1}\right.$$
$$\left. + \frac{(\bar{\ell}^b+1)^3}{2\bar{\ell}^b+1}\right] . \tag{5.2-6}$$

The important point to note is that while $\Delta\epsilon(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$ is of order $\hbar$, both sums are of order $\hbar^2$. The reason for this is that $\Delta\epsilon(\bar{\ell}^a\bar{\ell}^b\bar{\ell}^a{+}1\ \bar{\ell}^b)$ and $\Delta\epsilon(\bar{\ell}^a\bar{\ell}^b\bar{\ell}^a{-}1\ \bar{\ell}^b)$ almost cancel in the sum in Eq. 5.2-5. Their sum is a term of order $\hbar^2$.

Now let us expand the quantity $\eta'_{\lambda+1}(\mathcal{H}\sigma)$ appearing in the expression for $\mathcal{I}_{\mathrm{one}}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|0)_2$,

$$\eta'_{\lambda+1}(\mathcal{H}\sigma) = \eta'(L+\hbar, \bar{E}+\Delta E, \hbar) = \frac{1}{\hbar}\eta^{(0)\prime}(L,\bar{E})$$

$$+\frac{1}{\hbar}\frac{\partial\eta^{(0)\prime}}{\partial\bar{E}}(L,\bar{E})\,\Delta E + \frac{\partial\eta^{(0)\prime}}{\partial L}(L,\bar{E}) + \eta^{(1)\prime}(L,\bar{E}) + \cdots, \tag{5.2-7}$$

From Eqs. 5.1-24, 5.1-25, and 5.1-26 we see that the first term in this series is of zero order in $\hbar$, and that the second, third, and fourth terms are of first order. When these quantities, together with the expansion

$$\frac{\mathcal{H}}{\bar{\mathcal{H}}} = \frac{\gamma}{\bar{\gamma}} = 1 - \frac{1}{2}\frac{\Delta\epsilon}{\bar{\gamma}^2} + \cdots \tag{5.2-8}$$

are inserted into Eq. 4.3-1 and the summation over λ is carried out by again changing to an integral over b, we find that

$$I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|0)_2 = \frac{1}{\hbar^2} f_0(\bar{E}) + \frac{1}{\hbar^2} f_1(\bar{E})\Delta\epsilon$$

$$+ \frac{1}{\hbar} f_2(\bar{E}) + \cdots, \tag{5.2-9}$$

where f_0, f_1, and f_2 are functions of $\bar{E}$ only. The term $\hbar^{-2} f_0$ results from the insertion of the first term in Eq. 5.2-7 into the equation for $I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|0)_2$, $\hbar^{-2} f_1 \Delta\epsilon$ from the second term, and $\hbar^{-1} f_2$ from the third and fourth terms. When the terms containing f_0 and f_1 are inserted into the expression for $\mathcal{g}$, Eq. 5.2-1, and the summations over ℓ^a and ℓ^b are carried out by means of Eqs. 5.2-5 and 5.2-6 we obtain terms of zero order in $\hbar$. But when the term containing f_2 is inserted we obtain a term of order $\hbar$. Hence this term, though of the same order in $\hbar$ as the second term, may be neglected. It is for this reason that we never need to know $\eta^{(1)}$ explicitly. In the following work such terms, which do not contribute to the transport coefficients in the classical limit, will be omitted from the power series expansions.

We now present the results of carrying out these processes on $I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$. For J equal to zero and one, we have

$$I_{inel}(\bar{l}^a\bar{l}^b l^a l^b|0)_2 = \frac{1}{6}\,\frac{kT\sigma^4}{\hbar^2}\,(\bar{\gamma}^2-\Delta\epsilon)$$

$$\times\left\{\left(S^{l\bar{l}^a}_{l^a00}\right)^2\delta_{l^b\bar{l}^b}+\left(S^{l\bar{l}^b}_{l^b00}\right)^2\delta_{l^a\bar{l}^a}\right\}+\cdots, \tag{5.2-10}$$

and

$$I_{inel}(\bar{l}^a\bar{l}^b l^a l^b|1)_2 = -\frac{1}{6}\,\frac{kT\sigma^4}{\hbar^2}\,(\bar{\gamma}^2-\Delta\epsilon)$$

$$\times\left\{\left(S^{l\bar{l}^a}_{l^a00}\right)^2\delta_{l^b\bar{l}^b}+\left(S^{l\bar{l}^b}_{l^b00}\right)^2\delta_{l^a\bar{l}^a}\right\}+\cdots. \tag{5.2-11}$$

Only the term of order $\hbar^{-2}$ is required in the expansion of $I_{inel}(\bar{l}^a\bar{l}^b l^a l^b|2)_2$. It is found to be zero,

$$I_{inel}(\bar{l}^a\bar{l}^b l^a l^b|2)_2 = \frac{1}{\hbar^2}\,0+\cdots. \tag{5.2-12}$$

We must now obtain similar expansions for $g^{(1)}(\bar{l}^a\bar{l}^b l^a l^b)$ and $g^{(2)}(\bar{l}^a\bar{l}^b l^a l^b)$.

Section 5.3 The Expansion of $g^{(1)}(\bar{l}^a\bar{l}^b l^a l^b)$ and $g^{(2)}(\bar{l}^a\bar{l}^b l^a l^b)$ in Powers of $\hbar$.

The expansions of $Q^{(1)}(\bar{l}^a\bar{l}^b l^a l^b)_0$ and $Q^{(2)}(\bar{l}^a\bar{l}^b l^a l^b)_0$ have been obtained in Eqs. 5.1-30 and 5.1-31. Expressions for $Q^{(1)}_{el,A+B+C,}(\bar{l}^a\bar{l}^b l^a l^b)_2$ and $Q^{(2)}_{el,A+B+C,}(\bar{l}^a\bar{l}^b l^a l^b)_2$ are given in Eqs. 4.2-13 and 4.2-14 respectively. When these are expanded in powers of h we find that

$$Q^{(1)}_{ee,A+B+C_1}(\bar{e}^a\bar{e}^b e^a e^b)_2 = -\frac{4\pi}{3}\sigma^2\delta_{e^a\bar{e}^a}\delta_{e^b\bar{e}^b} + O(h), \qquad (5.3\text{-}1)$$

(5.3-1)

and

$$Q^{(2)}_{ee,A+B+C_1}(\bar{e}^a\bar{e}^b e^a e^b)_2 = -\frac{8\pi}{9}\sigma^2\delta_{e^a\bar{e}^a}\delta_{e^b\bar{e}^b} + O(h). \qquad (5.3\text{-}2)$$

Finally, we wish to carry out a similar expansion for $q^{(1)}_{ee,C_2}(\bar{e}^a\bar{e}^b e^a e^b)_2$, $q^{(2)}_{ee,C_2}(\bar{e}^a\bar{e}^b e^a e^b)_2$, $Q^{(1)}_{inel}(\bar{e}^a\bar{e}^b e^a e^b)_2$, and $Q^{(2)}_{inel}(\bar{e}^a\bar{e}^b e^a e^b)_2$. These are given by Eqs. 4.2-11, 4.2-12, 4.3-4, and 4.3-5 respectively. An expansion of the sum of $q^{(1)}_{ee,C_2}(\bar{e}^a\bar{e}^b e^a e^b)_2$ and $Q^{(1)}_{inel}(\bar{e}^a\bar{e}^b e^a e^b)_2$ will contain terms in $\Delta\epsilon$ due to the difference between $\mathcal{H}$ and $\overline{\mathcal{H}}$, and also terms arising from the different values of λ which occur. The terms in $\Delta\epsilon$ are obtained by making expansions such as that in Eq. 5.2-7 and carrying terms through second order in $\Delta\epsilon$. If we evaluate these terms again by changing the sum over λ to an integral over b we find that

$$g^{(1)}_{\ell\ell,c_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2 + Q^{(1)}_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b) = \Big[g^{(1)}_{\ell\ell,c_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2$$

$$+ Q^{(1)}_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2\Big]_{\mathcal{H}=\bar{\mathcal{H}}} - \frac{2\pi}{9}\,\frac{kT\sigma^4}{\hbar^2}\left(\Delta\epsilon - \frac{3}{8}\,\frac{\Delta\epsilon^2}{\gamma^2}\right)$$

$$\times \left\{\left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2 \delta_{\ell^b\bar{\ell}^b} + \left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2 \delta_{\ell^a\bar{\ell}^a}\right\} . \qquad (5.3\text{-}3)$$

The notation $[\quad]_{\mathcal{H}=\bar{\mathcal{H}}}$ means that the quantity in the brackets is to be evaluated at $\mathcal{H} = \bar{\mathcal{H}}$. While the lowest order terms in both $\left[g^{(1)}_{\ell\ell,c_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2\right]_{\mathcal{H}=\bar{\mathcal{H}}}$ and $\left[Q^{(1)}_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2\right]_{\mathcal{H}=\bar{\mathcal{H}}}$ are of order $\hbar^{-2}$, the terms of order $\hbar^{-2}$ and $\hbar^{-1}$ cancel in the sum; hence the sum is of zero order in $\hbar$. It is for this reason that we evaluate these terms together.

If we combine Eqs. 4.2-11 and 4.3-4 we find, after considerable manipulation, that

$$
\left[g^{(1)}_{el,c_2} (\bar{e}^a \bar{e}^b e^a e^b)_2 + Q^{(1)}_{inel} (\bar{e}^a \bar{e}^b e^a e^b)_2 \right]_{H=\bar{H}}
$$

$$
= \frac{2\pi}{3} \sigma^2 \left\{ \left(S^{1\bar{e}^a}_{e^a 00} \right)^2 \delta_{e^b \bar{e}^b} + \left(S^{1\bar{e}^b}_{e^b 00} \right)^2 \delta_{e^a \bar{e}^a} \right\}
$$

$$
\times \sum_{\lambda} \Bigg\{ (\lambda+1) \Bigg[\frac{\lambda+1}{2\lambda+3} \left(\eta'_{\lambda+1} \frac{\eta''_{\lambda}}{\eta'_{\lambda}} - \eta'_{\lambda} \frac{\eta''_{\lambda-1}}{\eta'_{\lambda-1}} \right) + \frac{\lambda+2}{2\lambda+3} \left(\eta'_{\lambda+1} \frac{\eta''_{\lambda+2}}{\eta'_{\lambda+2}} \right.
$$

$$
\left. - \eta'_{\lambda} \frac{\eta''_{\lambda+1}}{\eta'_{\lambda+1}} \right) + \frac{1}{(2\lambda+1)(2\lambda+3)} \eta'_{\lambda} \left(\frac{\eta''_{\lambda-1}}{\eta'_{\lambda-1}} - \frac{\eta''_{\lambda+1}}{\eta'_{\lambda+1}} \right) \Bigg] \sin 2(\eta_{\lambda+1} - \eta_{\lambda})
$$

$$
+ \frac{2\lambda^2}{2\lambda+1} \left[\sqrt{\eta'_{\lambda+1}} \cos(\eta_{\lambda+1} - \eta_{\lambda}) - \sqrt{\eta'_{\lambda-1}} \cos(\eta_{\lambda} - \eta_{\lambda-1}) \right]^2 \eta'_{\lambda}
$$

$$
- \frac{2\lambda^2}{2\lambda+1} \left[\sqrt{\eta'_{\lambda+1}} \sin(\eta_{\lambda+1} - \eta_{\lambda}) - \sqrt{\eta'_{\lambda-1}} \sin(\eta_{\lambda} - \eta_{\lambda-1}) \right]^2 \eta'_{\lambda}
$$

$$
+ \frac{2\lambda(\lambda+1)}{2\lambda+1} \left[\sqrt{\eta'_{\lambda+1}} \cos(\eta_{\lambda} - \eta_{\lambda-1}) - \sqrt{\eta'_{\lambda-1}} \cos(\eta_{\lambda+1} - \eta_{\lambda}) \right]^2 \eta'_{\lambda}
$$

$$
- \frac{2\lambda(\lambda+1)}{2\lambda+1} \left[\sqrt{\eta'_{\lambda+1}} \sin(\eta_{\lambda} - \eta_{\lambda-1}) - \sqrt{\eta'_{\lambda-1}} \sin(\eta_{\lambda+1} - \eta_{\lambda}) \right]^2 \eta'_{\lambda}
$$

$$
+ \frac{4\lambda}{(2\lambda+1)(2\lambda+3)} \eta'_{\lambda} \eta'_{\lambda+1} + \frac{2}{2\lambda+1} \eta'_{\lambda} \sqrt{\eta'_{\lambda-1} \eta'_{\lambda+1}} \cos(\eta_{\lambda+1} - \eta_{\lambda-1})
$$

$$
+ 2\eta'_{\lambda} \left[\eta'_{\lambda+1} \cos 2(\eta_{\lambda+1} - \eta_{\lambda}) - 2\sqrt{\eta'_{\lambda-1} \eta'_{\lambda+1}} \cos(\eta_{\lambda+1} - \eta_{\lambda-1}) \right] \Bigg\}.
\tag{5.3-4}
$$

Two problems are encountered when we attempt to evaluate the expression in Eq. 5.3-4 using the Euler-Maclaurin formula. When we expand the first term in the summation in Eq. 5.3-4, we have, to lowest order in $\hbar$,

$$\eta'_{\lambda+1}\frac{\eta''_{\lambda}}{\eta'_{\lambda}}-\eta'_{\lambda}\frac{\eta''_{\lambda-1}}{\eta'_{\lambda-1}}=\frac{\partial\eta^{(0)''}}{\partial L}. \tag{5.3-5}$$

However, the expression for $\frac{\partial\eta^{(0)''}}{\partial L}$ obtained by differentiating Eq. 5.1-19 is

$$\frac{\partial\eta^{(0)''}}{\partial L}=\frac{\hbar^2 b}{\sigma^3 E}\frac{\left(\frac{b^2}{\sigma^2}-2\right)}{\left(1-\frac{b^2}{\sigma^2}\right)^{\frac{3}{2}}}. \tag{5.3-6}$$

This is infinite for b equal to σ , whereas we would expect from continuity considerations that $\frac{\partial\eta^{(0)''}}{\partial L}$ equals zero at b equal to σ . The difficulty can be attributed to the fact that at b equals σ , the order and argument of the Bessel functions become equal. The asymptotic series which we use are not valid in this region. We may circumvent this difficulty by the following procedure. Consider an expansion of $Q^{(1)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_0$ in powers of $\hbar$. Thus

$$Q^{(1)}(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_0=Q^{(1)}_{classical}+\hbar Q^{(1)}_1(\bar{\ell}^{a}\bar{\ell}^{b}\ell^{a}\ell^{b})_0+\cdots. \tag{5.3-7}$$

If we multiply by $\mathcal{H}^2$ and differentiate twice with respect to $\mathcal{H}$ we find that, to lowest order in h ,

$$\frac{d^2}{d\mathcal{H}^2}\left[\mathcal{H}^2 Q^{(1)}(\bar{e}^a\bar{e}^b e^a e^b)_0\right] = 2Q^{(1)}_{classical} = 2\pi\sigma^2 \delta_{e^a\bar{e}^a}\delta_{e^b\bar{e}^b}. \tag{5.3-8}$$

But by differentiating Eq. 4.1-19 we obtain

$$\frac{d^2}{d\mathcal{H}^2}\left[\mathcal{H}^2 Q^{(1)}(\bar{e}^a\bar{e}^b e^a e^b)_0\right] = 4\pi\sigma^2 \delta_{e^a\bar{e}^a}\delta_{e^b\bar{e}^b}$$

$$\times \sum_\lambda (\lambda+1)(\eta''_{\lambda+1}-\eta''_\lambda)\sin 2(\eta_{\lambda+1}-\eta_\lambda)$$
$$+ 8\pi\sigma^2 \delta_{e^a\bar{e}^a}\delta_{e^b\bar{e}^b} \sum_\lambda (\lambda+1)(\eta'_{\lambda+1}-\eta'_\lambda)^2 \cos 2(\eta_{\lambda+1}-\eta_\lambda). \tag{5.3-9}$$

Combining the last two equations we find that

$$\sum_\lambda (\lambda+1)(\eta''_{\lambda+1}-\eta''_\lambda)\sin 2(\eta_{\lambda+1}-\eta_\lambda)$$

$$= \frac{1}{2} - 2\sum_\lambda (\lambda+1)(\eta'_{\lambda+1}-\eta'_\lambda)^2 \cos 2(\eta_{\lambda+1}-\eta_\lambda). \tag{5.3-10}$$

We may use this relation to eliminate the derivative $\frac{\partial\eta''}{\partial L}$.

Considering now the first two terms in the summation over λ in Eq. 5.3-4, we have

$$\sum_\lambda (\lambda+1)\left[\frac{\lambda+1}{2\lambda+3}\left(\eta'_{\lambda+1}\frac{\eta''_\lambda}{\eta'_\lambda} - \eta'_\lambda\frac{\eta''_{\lambda-1}}{\eta'_{\lambda-1}}\right)\right.$$

$$\left.+\frac{\lambda+2}{2\lambda+3}\left(\eta'_{\lambda+1}\frac{\eta''_{\lambda+2}}{\eta'_{\lambda+2}} - \eta'_\lambda\frac{\eta''_{\lambda+1}}{\eta'_{\lambda+1}}\right)\right]\sin 2(\eta_{\lambda+1}-\eta_\lambda)$$

$$= \sum_\lambda (\lambda+1)(\eta''_{\lambda+1} - \eta''_\lambda)\sin 2(\eta_{\lambda+1}-\eta_\lambda) + \cdots$$

$$= \frac{1}{2} - 2\sum_\lambda (\lambda+1)(\eta'_{\lambda+1}-\eta'_\lambda)^2\cos 2(\eta_{\lambda+1}-\eta_\lambda) + \cdots . \tag{5.3-11}$$

The term

$$\frac{\lambda+1}{(2\lambda+1)(2\lambda+3)}\eta'_\lambda\left(\frac{\eta''_{\lambda-1}}{\eta'_{\lambda-1}} - \frac{\eta''_{\lambda+1}}{\eta'_{\lambda+1}}\right)\sin 2(\eta_{\lambda+1}-\eta_\lambda) \tag{5.3-12}$$

is of at least first order in $\hbar$ and hence does not contribute to the classical limit. The four squared terms in brackets which follow are, to lowest order in $\hbar$, equal to

$$(\lambda+1)\left[2\left(\frac{\partial\eta'}{\partial L}\right)^2 - \frac{1}{2}\eta'^2\left(\frac{\partial\chi}{\partial L}\right)^2\right]\cos\chi, \tag{5.3-13}$$

where

$$\chi = 2\frac{\partial\eta}{\partial t}. \tag{5.3-14}$$

The sum over λ of the following two terms is

$$\sum_{\lambda}\left[\frac{4\lambda}{(2\lambda+1)(2\lambda+3)}\eta_{\lambda}'\eta_{\lambda+1}' + \frac{2}{2\lambda+1}\eta_{\lambda}'\sqrt{\eta_{\lambda-1}'\eta_{\lambda+1}'}\cos(\eta_{\lambda+1}-\eta_{\lambda-1})\right]. \tag{5.3-15}$$

Here occurs the second of the problems which were mentioned at the beginning of this section. If we were simply to change the sum over λ to an integral over b we would not be correct. The reason is that whenever there is a higher power of λ in the denominator than in the numerator all of the Euler-Maclaurin correction terms must be included. For example, consider the sum

$$\sum_{\lambda=0}^{\infty}\left(\frac{1}{\lambda+1} - \frac{1}{\lambda+2}\right). \tag{5.3-16}$$

If we were to change this sum to an integral, and neglect the 1 and the 2 in comparison with the λ we would obtain zero, whereas the value of the sum is actually equal to one. Hence, sums with higher powers of λ in the denominator than in the numerator must be carried out explicitly.

The final term in Eq. 5.3-4 is

$$2\eta_\lambda'\left[\eta_{\lambda+1}'\cos 2(\eta_{\lambda+1}-\eta_\lambda)-\sqrt{\eta_{\lambda-1}'\eta_{\lambda+1}'}\cos(\eta_{\lambda+1}-\eta_{\lambda-1})\right]. \qquad (5.3\text{-}17)$$

To lowest order in h this can be written as

$$h\left[\eta'\frac{\partial\eta'}{\partial L}\cos\chi-\frac{1}{2}\eta'^2\frac{\partial\chi}{\partial L}\sin\chi\right]. \qquad (5.3\text{-}18)$$

Since all terms are now of zero order in h, we may replace η and its derivatives by $h^{-1}\eta^{(0)}$ and the corresponding derivatives. When all these terms are inserted into Eq. 5.3-4, and the sum over λ is changed to an integral over b in those terms in which it is permissible to do so, we obtain

$$\left[q^{(1)}_{\mathscr{R},C_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2+Q^{(1)}_{\mathrm{line}}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2\right]_{\mathscr{H}=\bar{\mathscr{H}}}$$

$$=\frac{2\pi}{3}\sigma^2\left\{\left(S^{1\bar{\ell}^a}_{\ell^a00}\right)^2\delta_{\ell^b\bar{\ell}^b}+\left(S^{1\bar{\ell}^b}_{\ell^b00}\right)^2\delta_{\ell^a\bar{\ell}^a}\right\}$$

$$\times\left[\frac{1}{2}+\frac{1}{\sigma}\int_0^\sigma\left(-14\frac{b^3}{\sigma^3}+10\frac{b}{\sigma}\right)db\right.$$

$$+\sum_{\lambda=0}^{\infty}\left(\frac{1}{2\lambda+3}-\frac{1}{2\lambda+1}\right)\Bigg]$$

$$=\frac{2\pi}{3}\sigma^2\left\{\left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2\delta_{\ell^b\bar{\ell}^b}+\left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2\delta_{\ell^a\bar{\ell}^a}\right\}. \tag{5.3-19}$$

We must now carry out the same process on the sum $q^{(2)}_{el,C_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2 + Q^{(2)}_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2$. These quantities are given by Eqs. 4.2-12 and 4.3-5. As we did in the case of $q^{(1)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$ we write

$$q^{(2)}_{el,C_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2 + Q^{(2)}_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2 = \Big[q^{(2)}_{el,C_2}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2$$

$$+Q^{(2)}_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)_2\Big]_{\mathcal{H}=\mathcal{H}}+\frac{\pi}{18}\frac{kT\sigma^4}{\hbar^2}\frac{(\Delta\epsilon)^2}{\gamma^2}$$

$$\times\left\{\left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2\delta_{\ell^b\bar{\ell}^b}+\left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2\delta_{\ell^a\bar{\ell}^a}\right\}, \tag{5.3-20}$$

where the term in $(\Delta\epsilon)^2$ has been obtained in a straightforward fashion. The first term is given by

$$\left[q^{(2)}_{el,C_2} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2 + Q^{(2)}_{inel} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2 \right]_{\varkappa = \bar{\varkappa}}$$

$$= \frac{2\pi}{3} \sigma^2 \left\{ \left(S^{,\bar{\ell}^a}_{\ell^a 00}\right)^2 \delta_{\ell^b \bar{\ell}^b} + \left(S^{,\bar{\ell}^b}_{\ell^b 00}\right)^2 \delta_{\ell^a \bar{\ell}^a} \right\}$$

$$\times \sum_\lambda \left[\!\left[\frac{(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)} \left[\lambda \left(\eta'_{\lambda+2} \frac{\eta''_{\lambda+1}}{\eta'_{\lambda+1}} - \eta'_\lambda \frac{\eta''_{\lambda-1}}{\eta'_{\lambda-1}} \right) \right.\right.\right.$$

$$+ (\lambda+1) \left(\eta'_{\lambda+2} \frac{\eta''_{\lambda+3}}{\eta'_{\lambda+3}} - \eta'_\lambda \frac{\eta''_{\lambda+1}}{\eta'_{\lambda+1}} \right) + \frac{2}{2\lambda+5} \eta'_{\lambda+2} \left(\frac{\eta''_{\lambda+1}}{\eta'_{\lambda+1}} \right.$$

$$\left.\left. - \frac{\eta''_{\lambda+3}}{\eta'_{\lambda+3}} \right) \right] \sin 2(\eta_{\lambda+2} - \eta_\lambda)$$

$$+ \frac{2\lambda(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)} \left\{ \left[\sqrt{\eta'_\lambda \eta'_{\lambda-1}} \cos(\eta_{\lambda+2} - \eta_\lambda) - \sqrt{\eta'_{\lambda+1} \eta'_{\lambda+2}} \cos(\eta_{\lambda+1} - \eta_{\lambda-1}) \right]^2 \right.$$

$$+ \left[\sqrt{\eta'_{\lambda+1} \eta'_{\lambda+2}} \cos(\eta_{\lambda+2} - \eta_\lambda) - \sqrt{\eta'_\lambda \eta'_{\lambda-1}} \cos(\eta_{\lambda+1} - \eta_{\lambda-1}) \right]^2$$

$$- \left[\sqrt{\eta'_\lambda \eta'_{\lambda-1}} \sin(\eta_{\lambda+2} - \eta_\lambda) - \sqrt{\eta'_{\lambda+1} \eta'_{\lambda+2}} \sin(\eta_{\lambda+1} - \eta_{\lambda-1}) \right]^2$$

$$-\left[\sqrt{\eta_{\lambda+1}'\eta_{\lambda+2}'}\sin(\eta_{\lambda+2}-\eta_\lambda)-\sqrt{\eta_\lambda'\eta_{\lambda-1}'}\sin(\eta_{\lambda+1}-\eta_{\lambda-1})\right]^2\Bigg\}$$

$$+\frac{8(2\lambda^2+4\lambda-1)(\lambda+1)}{(2\lambda-1)(2\lambda+1)(2\lambda+3)(2\lambda+5)}\eta_\lambda'\eta_{\lambda+1}'$$

$$+\frac{4(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)(2\lambda+5)}\eta_{\lambda+1}'(\eta_\lambda'+\eta_{\lambda+2}')\cos 2(\eta_{\lambda+2}-\eta_\lambda)$$

$$+\frac{16(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)(2\lambda+5)}\eta_{\lambda+1}'\sqrt{\eta_\lambda'\eta_{\lambda+2}'}\cos(\eta_{\lambda+2}-\eta_\lambda)\Bigg]\Bigg].$$

(5.3-21)

In order to remove the terms in η'' in this expression we use the following equation, which is derived in a manner analogous to that used in the derivation of Eq. 5.3-10.

$$\sum_\lambda \frac{(\lambda+1)(\lambda+2)}{(2\lambda+3)}(\eta_{\lambda+2}''-\eta_\lambda'')\sin 2(\eta_{\lambda+2}-\eta_\lambda)$$

$$=\frac{1}{3}-2\sum_\lambda \frac{(\lambda+1)(\lambda+2)}{(2\lambda+3)}(\eta_{\lambda+2}'-\eta_\lambda')^2$$

$$\times\cos 2(\eta_{\lambda+2}-\eta_\lambda). \qquad (5.3\text{-}22)$$

Then, after carrying out manipulations similar to those performed in obtaining $\left[g^{(1)}_{\ell\ell, C_2}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2 + Q^{(1)}_{\mathrm{inel}}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)\right]_{\mathcal{H}=\bar{\mathcal{H}}}$ we find

$$\left[g^{(2)}_{\ell\ell, C_2}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2 + Q^{(2)}_{\mathrm{inel}}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2\right]_{\mathcal{H}=\bar{\mathcal{H}}}$$

$$= \frac{2\pi}{3}\sigma^2 \left\{ \left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2 \delta_{\ell^b \bar{\ell}^b} + \left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2 \delta_{\ell^a \bar{\ell}^a} \right\}$$

$$\times \left[\frac{1}{3} + \frac{1}{\sigma}\int_0^\sigma \left(-40\frac{b^5}{\sigma^5} + 44\frac{b^3}{\sigma^3} - 8\frac{b}{\sigma}\right) db \right.$$

$$\left. + 8 \sum_{\lambda=0}^{\infty} \frac{\lambda^2 + 2\lambda + 1}{(2\lambda-1)(2\lambda+1)(2\lambda+3)(2\lambda+5)} \right]. \qquad (5.3\text{-}23)$$

The integral over b appearing in this expression is equal to 1/3, and the sum over λ is equal to zero. This can be seen from the fact that

$$\sum_{\lambda=0}^{\infty} \frac{\lambda^2 + 2\lambda + 1}{(2\lambda-1)(2\lambda+1)(2\lambda+3)(2\lambda+5)}$$

$$= \frac{1}{64} \sum_{\lambda=0}^{\infty} \left(\frac{3}{2\lambda-1} - \frac{1}{2\lambda+1} + \frac{1}{2\lambda+3} - \frac{3}{2\lambda+5} \right)$$

$$= 0. \qquad (5.3\text{-}24)$$

The sum is carried out by noting that all terms in each series cancel with terms in other series except the first few. These must be added explicitly. Thus we find that

$$\left[g^{(2)}_{\ell\ell, c_2} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2 + Q^{(2)}_{line} (\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)_2 \right]_{\mathcal{H}=\bar{\mathcal{H}}}$$

$$= \frac{4\pi}{9} \sigma^2 \left\{ \left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2 \delta_{\ell^b \bar{\ell}^b} + \left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2 \delta_{\ell^a \bar{\ell}^a} \right\} + \cdots \tag{5.3-25}$$

We have now completed the expansion of $g^{(1)}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)$ and $g^{(2)}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b)$. From Eqs. 5.1-30, 5.3-1, 5.3-3, and 5.3-19 we have

$$g^{(1)}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b) = \pi \sigma^2 \delta_{\ell^a \bar{\ell}^a} \delta_{\ell^b \bar{\ell}^b}$$

$$+ \delta^2 \left[- \frac{8\pi}{3} \delta_{\ell^a \bar{\ell}^a} \delta_{\ell^b \bar{\ell}^b} + \frac{4\pi}{3} \left\{ \left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2 \delta_{\ell^b \bar{\ell}^b} + \left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2 \delta_{\ell^a \bar{\ell}^a} \right\} \right.$$

$$- \frac{2\pi}{9} \frac{kT\sigma^2}{h^2} \left(\Delta\epsilon - \frac{3}{8} \frac{\Delta\epsilon^2}{\gamma^2} \right) \left\{ \left(S^{1\bar{\ell}^a}_{\ell^a 00}\right)^2 \delta_{\ell^b \bar{\ell}^b} \right.$$

$$\left. \left. + \left(S^{1\bar{\ell}^b}_{\ell^b 00}\right)^2 \delta_{\ell^a \bar{\ell}^a} \right\} + \cdots \right] + \cdots \tag{5.3-26}$$

From Eqs. 5.1-31, 5.3-2, 5.3-20, and 5.3-25, we have

$$g^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b) = \frac{2}{3}\pi\sigma^2\,\delta_{\ell^a\bar{\ell}^a}\,\delta_{\ell^b\bar{\ell}^b}$$

$$+\delta^2\Big[-\frac{8\pi}{9}\delta_{\ell^a\bar{\ell}^a}\delta_{\ell^b\bar{\ell}^b}+\frac{4\pi}{9}\Big\{\big(S^{1\bar{\ell}^a}_{\ell^a00}\big)^2\delta_{\ell^b\bar{\ell}^b}+\big(S^{1\bar{\ell}^b}_{\ell^b00}\big)^2\delta_{\ell^a\bar{\ell}^a}\Big\}$$

$$+\frac{\pi}{18}\frac{kT\sigma^2}{\hbar^2}\frac{(\Delta\epsilon)^2}{\bar{\delta}^2}\Big\{\big(S^{1\bar{\ell}^a}_{\ell^a00}\big)^2\delta_{\ell^b\bar{\ell}^b}+\big(S^{1\bar{\ell}^b}_{\ell^b00}\big)^2\delta_{\ell^a\bar{\ell}^a}\Big\}$$

$$+\cdots\Big]+\cdots. \qquad (5.3\text{-}27)$$

The expansions of $I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|J)_2$ for J equal to 0, 1, and 2 are also needed in the evaluation of the classical limit of the transport coefficients. They are given by Eqs. 5.2-10, 5.2-11, and 5.2-12 respectively.

This completes the expansion of the moments of the cross section of Chapter IV in powers of $\hbar$. Again it should be emphasized that only those terms have been evaluated which contribute to the classical limit of the transport coefficients. We shall now proceed to the evaluation of these coefficients.

CHAPTER VI

THE TRANSPORT COEFFICIENTS

We have now arrived at the last step in our development, the evaluation of the classical limit of the transport coefficients. The formulas which we use for these coefficients were first derived by Wang Chang, Uhlenbeck, and de Boer[20,21]. As mentioned in Chapter I, McCourt and Snider[25] have recently shown that these formulas are correct if the degeneracy averaged cross section is used; also, in sums over internal states the degeneracy of the state must be included. We use the formulas in the form developed by Mason and Monchick[37].

Section 6.1 The Relaxation Time

Since a loaded sphere has two internal degrees of freedom (only two need be considered since the angular velocity about the symmetry axis cannot be changed in a collision), the quantity

$$\frac{2}{3}\,\mathcal{U}^{(tr)} - \mathcal{U}^{(rot)} \tag{6.1-1}$$

approaches zero as time progresses. Here $\mathcal{U}^{(tr)}$ and $\mathcal{U}^{(rot)}$ are the mean translational and rotational energies per molecule (excluding any energy associated with rotation about the symmetry axis). If the system is only slightly displaced from equilibrium, this quantity decreases to a value 1/e of its original value in a time τ called the relaxation time. The expression given by Mason and Monchick for this quantity is

$$\frac{1}{\tau} = \frac{2nk}{C^{(int)}}\sqrt{\frac{kT}{\pi m}}\left[\sum_{\bar{\ell}^a}(2\bar{\ell}^a+1)e^{-\epsilon_{\bar{\ell}^a}}\right]^{-2}$$

$$\times \sum_{\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b}(\Delta\epsilon)^2(2\bar{\ell}^a+1)(2\bar{\ell}^b+1)e^{-\epsilon_{\bar{\ell}^a}-\epsilon_{\bar{\ell}^b}} \tag{6.1-2}$$

$$\times\int \bar{\gamma}^3 e^{-\bar{\gamma}^2} I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)\sin\chi\, d\chi\, d\varphi\, d\bar{\gamma},$$

where k is Boltzmann's constant; $C^{(int)}$ is the internal specific heat per molecule and is equal to k for the loaded sphere; n is the number density; and $\epsilon_{\bar{\ell}^a}$ is equal to $E_{\bar{\ell}^a}/kT$, where $E_{\bar{\ell}^a}$ is the internal energy in the state specified by the quantum number $\bar{\ell}^a$. The quantity $I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)$ is the degeneracy averaged cross section defined in Eq. 3.1-2.

From Eq. 3.1-3 it follows that

$$\int I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)\sin\chi\, d\chi\, d\varphi = 4\pi I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|0). \tag{6.1-3}$$

Due to the presence of the quantity $(\Delta\epsilon)^2$ in the integrand of Eq. 6.1-2, we need insert only the inelastic part of $I(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|0)$ into the integral, since the elastic terms make no contribution. Thus

$$\frac{1}{\tau} = 8\pi n \sqrt{\frac{kT}{\pi m}} \left(\frac{\delta}{\sigma}\right)^2 \left[\sum_{\bar{l}^a} (2\bar{l}^a+1) e^{-\epsilon_{\bar{l}^a}} \right]^{-2}$$

$$\sum_{\bar{l}^a \bar{l}^b l^a l^b} (\Delta\epsilon)^2 (2\bar{l}^a+1)(2\bar{l}^b+1) e^{-\epsilon_{\bar{l}^a} - \epsilon_{\bar{l}^b}}$$

$$\times \int \bar{\gamma}^3 e^{-\bar{\gamma}^2} I_{inel}(\bar{l}^a \bar{l}^b l^a l^b | 0)_2 \, d\bar{\gamma}. \tag{6.1-4}$$

This equation, together with the expression for the energy levels of the loaded sphere, Eq. 1.2-3, and the expression for $I_{inel}(\bar{l}^a \bar{l}^b l^a l^b | 0)_2$, Eq. 4.3-1, gives an exact quantum mechanical expression for the reciprocal of the relaxation time to second order in the parameter δ/σ.

We now proceed to find the classical limit of the relaxation time. Using the expression for the expansion of $I_{inel}(\bar{l}^a \bar{l}^b l^a l^b | 0)_2$ in powers of $\hbar$, Eq. 5.2-10, we find that

$$\frac{1}{\tau} = \frac{4\pi}{3} \frac{n \delta^2 \sigma^2 kT}{\hbar^2} \sqrt{\frac{kT}{\pi m}} \left[\sum_{\bar{l}^a} (2\bar{l}^a+1) e^{-\epsilon_{\bar{l}^a}} \right]^{-2}$$

$$\times \sum_{\bar{l}^a \bar{l}^b l^a l^b} (2\bar{l}^a+1)(2\bar{l}^b+1) e^{-\epsilon_{\bar{l}^a} - \epsilon_{\bar{l}^b}} (\Delta\epsilon)^2$$

$$\times \left\{ \left(S^{1\bar{l}^a}_{l^a 0 0}\right)^2 \delta_{l^b \bar{l}^b} + \left(S^{1\bar{l}^b}_{l^b 0 0}\right)^2 \delta_{l^a \bar{l}^a} \right\}. \tag{6.1-5}$$

In obtaining this result, we have carried out the integration over $\bar{\gamma}$ by means of the formula

$$\int_0^\infty \bar{\gamma}^n e^{-\bar{\gamma}^2} d\bar{\gamma} = \frac{1}{2}\left[\left(\frac{n-1}{2}\right)!\right]. \qquad (6.1\text{-}6)$$

To lowest order in $\hbar$ we have

$$\sum_{\bar{\ell}^a} (2\bar{\ell}^a+1) e^{-\epsilon_{\bar{\ell}^a}} = \int (2\bar{\ell}^a+1) e^{-\frac{\hbar^2 \bar{\ell}^a(\bar{\ell}^a+1)}{2\Gamma kT}} d\bar{\ell}^a$$

$$= \frac{2\Gamma kT}{\hbar^2} . \qquad (6.1\text{-}7)$$

Finally, we use Eq. 5.2-6 to carry out the sums over the final states, and carry out the sums over the initial states by again changing the sums to integrals. The result is

$$\left(\frac{1}{\tau}\right)_{C.L.} = \frac{16}{3} n \sqrt{\frac{kT}{\pi m}}\, \pi \sigma^2 \left(\frac{m\delta^2}{\Gamma}\right). \qquad (6.1\text{-}8)$$

The subscript C.L. denotes classical limit. This result will be compared with other values which have been obtained for the relaxation time for a gas of loaded spheres in Section 6.4.

Section 6.2 The Coefficient of Shear Viscosity

The formula which Mason and Monchick give for the coefficient of shear viscosity η is

$$\frac{1}{\eta} = \frac{8}{5\sqrt{\pi m k T}}\left[\sum_{\bar{\ell}^a}(2\bar{\ell}^a+1)e^{-\epsilon_{\bar{\ell}^a}}\right]^{-2}\sum_{\bar{\ell}^a\bar{\ell}^b\ell'^a\ell'^b}(2\bar{\ell}^a+1)(2\bar{\ell}^b+1)$$

$$\times e^{-\epsilon_{\bar{\ell}^a}-\epsilon_{\bar{\ell}^b}}\int\left[\bar{\gamma}^4\sin^2\chi+\frac{1}{3}(\Delta\epsilon)^2-\frac{1}{2}(\Delta\epsilon)^2\sin^2\chi\right]$$

$$\times\bar{\gamma}^3 e^{-\bar{\gamma}^2} I(\bar{\ell}^a\bar{\ell}^b\ell'^a\ell'^b)\sin\chi\, d\chi\, d\varphi\, d\bar{\gamma}. \quad (6.2\text{-}1)$$

We carry out the angle integrations, and obtain

$$\frac{1}{\eta} = \frac{8}{5\sqrt{\pi m k T}}\left[\sum_{\bar{\ell}^a}(2\bar{\ell}^a+1)e^{-\epsilon_{\bar{\ell}^a}}\right]^{-2}\sum_{\bar{\ell}^a\bar{\ell}^b\ell'^a\ell'^b}(2\bar{\ell}^a+1)$$

$$\times(2\bar{\ell}^b+1)e^{-\epsilon_{\bar{\ell}^a}-\epsilon_{\bar{\ell}^b}}\int\Big[\bar{\gamma}^4 g^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell'^a\ell'^b)$$

$$+\frac{4\pi}{15}(\Delta\epsilon)^2\left(\frac{\delta}{\sigma}\right)^2 I_{ines}(\bar{\ell}^a\bar{\ell}^b\ell'^a\ell'^b|2)_2\Big]\bar{\gamma}^3 e^{-\bar{\gamma}^2}\, d\bar{\gamma}.$$

(6.2-2)

Here we have substituted $g^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell'^a\ell'^b)$ for $Q^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell'^a\ell'^b)$ in accordance with the discussion given in Section 4.2. The quantity $g^{(2)}(\bar{\ell}^a\bar{\ell}^b\ell'^a\ell'^b)$ is equal to the following sum:

$$q^{(2)}(\bar{\ell}^{c}\bar{j}^{b}\ell^{c}j^{b}) = Q^{(2)}(\bar{\ell}^{c}\bar{j}^{b}\ell^{c}j^{b})_{0}$$

$$+\left(\frac{\delta}{\sigma}\right)^{2}\Big[Q^{(2)}_{el,A+B+C_1}(\bar{\ell}^{c}\bar{j}^{b}\ell^{c}j^{b})_{2} + q^{(2)}_{el,C_2}(\bar{\ell}^{c}\bar{j}^{b}\ell^{c}j^{b})_{2}$$

$$+ Q^{(2)}_{inel}(\bar{\ell}^{c}\bar{j}^{b}\ell^{c}j^{b})_{2}\Big] + \cdots \qquad (6.2\text{-}3)$$

The spherical term $Q^{(2)}(\bar{\ell}^{c}\bar{j}^{b}\ell^{c}j^{b})_{0}$ is given by Eq. 4.1-20; the elastic terms which are of second order in δ/σ, $Q^{(2)}_{el,A+B+C_1}(\bar{\ell}^{c}\bar{j}^{b}\ell^{c}j^{b})_{2}$ and $Q^{(2)}_{el,C_2}(\bar{\ell}^{c}\bar{j}^{b}\ell^{c}j^{b})_{2}$, are given by Eqs. 4.2-14 and 4.2-12; and the inelastic term which is of second order in δ/σ, $Q^{(2)}_{inel}(\bar{\ell}^{c}\bar{j}^{b}\ell^{c}j^{b})_{2}$, is given by Eq. 4.3-5. The quantity $I_{inel}(\bar{\ell}^{c}\bar{j}^{b}\ell^{c}j^{b}|2)_{2}$ is given by Eq. 4.3-3. Thus, by means of these formulas, one may obtain numerical values for the quantum mechanical coefficient of shear viscosity for a gas of loaded spheres through second order in δ/σ.

In order to calculate the classical limit of the coefficient of shear viscosity, we make use of the expansions of $q^{(2)}(\bar{\ell}^{c}\bar{j}^{b}\ell^{c}j^{b})$, Eq. 5.3-7, and $I_{inel}(\bar{\ell}^{c}\bar{j}^{b}\ell^{c}j^{b}|2)_{2}$, Eq. 5.2-12, in power series in $\hbar$. When these expressions are inserted into Eq. 6.2-2, and the sums over the internal states and the integration over $\bar{\gamma}$ are carried out, we obtain the result

$$\eta = \frac{5}{16} \frac{\sqrt{\pi m k T}}{\pi \sigma^2} \left(1 - \frac{1}{9} \frac{m \delta^2}{I}\right). \qquad (6.2\text{-}4)$$

We note that setting δ equal to zero yields the expression for the coefficient of shear viscosity for a gas of rigid spheres of diameter σ . This is, of course, to be expected from the definition of δ as a parameter which measures the degree to which the loaded sphere under consideration differs from an ordinary rigid sphere.

Section 6.3 <u>The Coefficient of Thermal Conductivity</u>

The coefficient of thermal conductivity λ is written as the sum of two terms,

$$\lambda = \lambda_{tr} + \lambda_{int}, \qquad (6.3\text{-}1)$$

where λ_{tr} arises from the flux of translational kinetic energy, and λ_{int} from the flux of internal energy. The expressions for these quantities are

$$\lambda_{tr}\left(1 - \frac{Y^2}{XZ}\right) = \frac{75}{8} \frac{k^2 T}{m} \frac{1}{X} + \frac{15}{4} \frac{k T c^{(int)}}{m} \left(\frac{Y}{XZ}\right).$$

and (6.3-2)

$$\lambda_{int}\left(1-\frac{Y^2}{XZ}\right)=\frac{3}{2}\,\frac{c^{(int)^2}T}{m}\,\frac{1}{Z}+\frac{15}{4}\,\frac{kTc^{(int)}}{m}\left(\frac{Y}{XZ}\right),$$

(6.3-3)

where

$$X=4\sqrt{\frac{kT}{\pi m}}\left[\sum_{\bar{l}^a}(2\bar{l}^a+1)e^{-\epsilon_{\bar{l}^a}}\right]^{-2}\sum_{\bar{l}^a\bar{l}^b l^a l^b}(2\bar{l}^a+1)$$

$$\times(2\bar{l}^b+1)e^{-\epsilon_{\bar{l}^a}-\epsilon_{\bar{l}^b}}\int\Big[\bar{\gamma}^4\sin^2\chi+\frac{11}{8}(\Delta\epsilon)^2$$

$$-\frac{1}{2}(\Delta\epsilon)^2\sin^2\chi\Big]\,\bar{\gamma}^3e^{-\bar{\gamma}^2}\,I(\bar{l}^a\bar{l}^b l^a l^b)$$

$$\times\sin\chi\, d\chi\, d\varphi\, d\bar{\gamma},$$ (6.3-4)

$$Y=\frac{5}{2}\sqrt{\frac{kT}{\pi m}}\left[\sum_{\bar{l}^a}(2\bar{l}^a+1)e^{-\epsilon_{\bar{l}^a}}\right]^{-2}$$

$$\times\sum_{\bar{l}^a\bar{l}^b l^a l^b}(\Delta\epsilon)^2(2\bar{l}^a+1)(2\bar{l}^b+1)e^{-\epsilon_{\bar{l}^a}-\epsilon_{\bar{l}^b}}$$

$$\times\int\bar{\gamma}^3e^{-\bar{\gamma}^2}I(\bar{l}^a\bar{l}^b l^a l^b)\sin\chi\, d\chi\, d\varphi\, d\bar{\gamma},$$

(6.3-5)

$$Z = 4\sqrt{\frac{kT}{\pi m}}\left[\sum_{\bar{l}^a}(2\bar{l}^a+1)e^{-\epsilon_{\bar{l}^a}}\right]^{-2}\sum_{\bar{l}^a\bar{l}^b l^a l^b}(\epsilon_{\bar{l}^a}-\langle\epsilon\rangle)$$

$$\times(2\bar{l}^a+1)(2\bar{l}^b+1)e^{-\epsilon_{\bar{l}^a}-\epsilon_{\bar{l}^b}}\int\Big[-\frac{3}{2}(\Delta\epsilon)+\bar{\gamma}^2(\epsilon_{\bar{l}^a}-\epsilon_{\bar{l}^b})$$

$$-\gamma\bar{\gamma}(\epsilon_{l^a}-\epsilon_{l^b})\cos\chi\Big]\bar{\gamma}^3 e^{-\bar{\gamma}^2} I(\bar{l}^a\bar{l}^b l^a l^b)$$

$$\times\sin\chi\, d\chi\, d\varphi\, d\bar{\gamma}, \tag{6.3-6}$$

and

$$\langle\epsilon\rangle = \sum_{\bar{l}^a}\epsilon_{\bar{l}^a}(2\bar{l}^a+1)e^{-\epsilon_{\bar{l}^a}} \Big/ \sum_{\bar{l}^a}(2\bar{l}^a+1)e^{-\epsilon_{\bar{l}^a}}. \tag{6.3-7}$$

It is shown by Mason and Monchick that the quantities X and Y can be written exactly in terms of the relaxation time and the coefficient of shear viscosity,

$$X = \frac{5}{2}\left(\frac{kT}{\eta}\right)+\frac{25}{12}\left(\frac{C^{(int)}}{nk\tau}\right), \tag{6.3-8}$$

and

$$Y = \frac{5}{4}\left(\frac{C^{(int)}}{nk\tau}\right). \tag{6.3-9}$$

The quantity Z may be written as the sum of three terms,

$$Z = Z_1 + Z_2 + Z_3 \ , \tag{6.3-10}$$

where

$$Z_1 = \frac{3}{4}\left(\frac{C^{(int)}}{nk\tau}\right), \tag{6.3-11}$$

$$Z_2 = 4\sqrt{\frac{kT}{\pi m}}\left[\sum_{\bar{\ell}^a}(2\bar{\ell}^a+1)e^{-\epsilon_{\bar{\ell}^a}}\right]^{-2}$$

$$\times \sum_{\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b}(\epsilon_{\bar{\ell}^a}-\langle\epsilon\rangle)(2\bar{\ell}^a+1)(2\bar{\ell}^b+1)e^{-\epsilon_{\bar{\ell}^a}-\epsilon_{\bar{\ell}^b}}(\epsilon_{\bar{\ell}^a}-\epsilon_{\bar{\ell}^b})$$

$$\times \int q^{(1)}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b)\,\bar{\gamma}^5 e^{-\bar{\gamma}^2}\,d\bar{\gamma}\ , \tag{6.3-12}$$

and

$$Z_3 = \frac{16}{3} \pi \sqrt{\frac{kT}{\pi m}} \left(\frac{\delta}{\sigma}\right)^2 \left[\sum_{\bar{l}^a} (2\bar{l}^a+1) e^{-\epsilon_{\bar{l}^a}} \right]^{-2}$$

$$\times \sum_{\bar{l}^a \bar{l}^b l^a l^b}{}' \left(\epsilon_{\bar{l}^a} - \langle \epsilon \rangle\right) (2\bar{l}^a+1)(2\bar{l}^b+1)\, e^{-\epsilon_{\bar{l}^a} - \epsilon_{\bar{l}^b}}$$

$$\times \int \left[\bar{\gamma} \left(\epsilon_{\bar{l}^a} - \epsilon_{\bar{l}^b}\right) - \gamma \left(\epsilon_{l^a} - \epsilon_{l^b}\right) \right]$$

$$\times \bar{\gamma}^4 e^{-\bar{\gamma}^2} I_{v.el}\left(\bar{l}^a \bar{l}^b l^a l^b \middle| 1\right)_2 d\bar{\gamma}. \qquad (6.3\text{-}13)$$

The expression for $g^{(1)}(\bar{l}^a \bar{l}^b l^a l^b)$ may be written in a manner analogous to that for $g^{(2)}(\bar{l}^a \bar{l}^b l^a l^b)$, Eq. 6.2-3. Thus

$$g^{(1)}(\bar{l}^a \bar{l}^b l^a l^b) = Q^{(1)}(\bar{l}^a \bar{l}^b l^a l^b)_0$$

$$+ \left(\frac{\delta}{\sigma}\right)^2 \left[Q^{(1)}_{el,A+B+C_1}(\bar{l}^a \bar{l}^b l^a l^b)_2 + g^{(1)}_{el,C_2}(\bar{l}^a \bar{l}^b l^a l^b)_2 \right.$$

$$\left. + Q^{(1)}_{inel}(\bar{l}^a \bar{l}^b l^a l^b)_2 \right] + \cdots \qquad (6.3\text{-}14)$$

where $Q^{(1)}(\bar{l}^a \bar{l}^b l^a l^b)_0$ is given by Eq. 4.1-19, the elastic terms $Q^{(1)}_{el,A+B+C_1}(\bar{l}^a \bar{l}^b l^a l^b)_2$ and $g^{(1)}_{el,C_2}(\bar{l}^a \bar{l}^b l^a l^b)_2$ are given by Eqs. 4.2-13 and 4.2-11, and the inelastic term $Q^{(1)}_{inel}(\bar{\ell}^{o}\bar{\ell}^{b}\ell^{o}\ell^{b})_2$ is given by Eq. 4.3-4. The quantity $I_{inel}(\bar{\ell}^{o}\bar{\ell}^{b}\ell^{o}\ell^{b}|1)_2$ is given by Eq. 4.3-2. Thus we have all of the quantities needed for an exact calculation of the translational and internal contributions to the thermal conductivity of a gas of loaded spheres, through second order in δ/σ .

In order to obtain the classical limits of these quantities, we make use of our results for the classical relaxation time and coefficient of shear viscosity to write

$$(X)_{c.l.} = 8\sqrt{\frac{kT}{\pi m}}\,\pi\sigma^2\left(1+\frac{3}{2}\,\frac{m\delta^2}{I}\right), \tag{6.3-15}$$

$$(Y)_{c.l.} = \frac{20}{3}\sqrt{\frac{kT}{\pi m}}\,\pi\sigma^2\left(\frac{m\delta^2}{I}\right), \tag{6.3-16}$$

and

$$(Z_1)_{c.l.} = 4\sqrt{\frac{kT}{\pi m}}\,\pi\sigma^2\left(\frac{m\delta^2}{I}\right). \tag{6.3-17}$$

When we insert the expansion of $g^{(1)}(\bar{\ell}^{o}\bar{\ell}^{b}\ell^{o}\ell^{b})$, Eq. 5.3-26, into the expression for Z_2 given by Eq. 6.3-12, and carry out the sums over the internal states and the integration over $\bar{\gamma}$, we obtain

$$(Z_2)_{c.l.} = 4\sqrt{\frac{kT}{\pi m}}\ \pi\sigma^2\left(1 - \frac{1}{9}\ \frac{m\delta^2}{\Gamma}\right). \qquad (6.3\text{-}18)$$

In order to find the classical limit of the quantity Z_3 , Eq. 6.3-13, we write

$$\gamma = \bar{\gamma} - \frac{1}{2}\ \frac{\Delta\epsilon}{\bar{\gamma}} - \frac{1}{8}\ \frac{(\Delta\epsilon)^2}{\bar{\gamma}^3} + \cdots, \qquad (6.3\text{-}19)$$

and

$$\epsilon_{\ell^a} = \epsilon_{\bar{\ell}^a} + \Delta\epsilon_{\bar{\ell}^a}\ , \qquad (6.3\text{-}20)$$

where $\Delta\epsilon_{\bar{\ell}^a}$ is the change in internal energy of molecule a . Then Z_3 may be written as the sum of two terms:

$$Z_3^{(1)} = -\frac{16\pi}{3}\sqrt{\frac{kT}{\pi m}}\left(\frac{\delta}{\sigma}\right)^2\left[\sum_{\bar{\ell}^a}(2\bar{\ell}^a+1)\,e^{-\epsilon_{\bar{\ell}^a}}\right]^{-2}$$

$$\times\sum_{\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b}(\epsilon_{\bar{\ell}^a} - \langle\epsilon\rangle)(2\bar{\ell}^a+1)(2\bar{\ell}^b+1)\,e^{-\epsilon_{\bar{\ell}^a}-\epsilon_{\bar{\ell}^b}}$$

$$\times(\Delta\epsilon_{\bar{\ell}^a} - \Delta\epsilon_{\bar{\ell}^b})\int\left(\bar{\gamma}^2 - \tfrac{1}{2}\Delta\epsilon\right)\bar{\gamma}^3 e^{-\bar{\gamma}^2}$$

$$\times I_{inel}(\bar{\ell}^a\bar{\ell}^b\ell^a\ell^b|1)_2\,d\bar{\gamma}, \qquad (6.3\text{-}21)$$

and

$$Z_3^{(2)} = \frac{8\pi}{3}\sqrt{\frac{kT}{\pi m}}\left(\frac{\delta}{\sigma}\right)^2 \left[\sum_{\bar{l}^a}(2\bar{l}^a+1)e^{-\epsilon_{\bar{l}^a}}\right]^{-2}$$

$$\times \sum_{\bar{l}^a\bar{l}^b l^a l^b}(\epsilon_{\bar{l}^a}-\langle\epsilon\rangle)(\epsilon_{\bar{l}^a}-\epsilon_{\bar{l}^b})(2\bar{l}^a+1)(2\bar{l}^b+1)e^{-\epsilon_{\bar{l}^a}-\epsilon_{\bar{l}^b}}$$

$$\times \int\left(\Delta\epsilon+\frac{1}{4}\frac{\Delta\epsilon^2}{\bar{\gamma}^2}\right)\bar{\gamma}^3 e^{-\bar{\gamma}^2} I_{inel}(\bar{l}^a\bar{l}^b l^a l^b|1)_2\, d\bar{\gamma}. \tag{6.3-22}$$

The classical limits of these expressions are found by inserting the expansion of $I_{inel}(\bar{l}^a\bar{l}^b l^a l^b|1)_2$ in powers of $\hbar$, Eq. 5.2-11, into the above expressions, and again carrying out the indicated sums and integration. The results obtained are

$$(Z_3^{(1)})_{c.l.} = -\frac{8}{3}\sqrt{\frac{kT}{\pi m}}\,\pi\sigma^2\left(\frac{m\delta^2}{I}\right), \tag{6.3-23}$$

and

$$(Z_3^{(2)})_{c.l.} = \frac{4}{9}\sqrt{\frac{kT}{\pi m}}\,\pi\sigma^2\left(\frac{m\delta^2}{I}\right). \tag{6.3-24}$$

When the separate contributions to Z are added, we find that

$$(Z)_{c.l.} = 4\sqrt{\frac{kT}{\pi m}}\ \pi\sigma^2\left(1+\frac{1}{3}\frac{m\delta^2}{\Gamma}\right). \tag{6.3-25}$$

Finally, we insert the values of $(X)_{c.l.}$, $(Y)_{c.l.}$, and $(Z)_{c.l.}$, given by Eqs. 6.3-15, 6.3-16, and 6.3-25, respectively into Eqs. 6.3-2 and 6.3-3 for the coefficients of thermal conductivity, and obtain

$$(\lambda_{tr})_{c.l.} = \frac{75}{64}\ \frac{\sqrt{\pi m kT}}{\pi\sigma^2}\ \frac{k}{m}\left(1-\frac{5}{6}\frac{m\delta^2}{\Gamma}\right), \tag{6.3-26}$$

and

$$(\lambda_{int})_{c.l.} = \frac{3}{8}\ \frac{\sqrt{\pi m kT}}{\pi\sigma^2}\ \frac{k}{m}\left(1+\frac{7}{4}\frac{m\delta^2}{\Gamma}\right). \tag{6.3-27}$$

This completes the evaluation of the classical limits of the transport coefficients.

Section 6.4 Discussion

The first calculation of a transport property for the loaded sphere model was made by J. Jeans[11,12]. Using the mean free path approach to kinetic theory, he obtained the following result for the relaxation time:

$$\left(\frac{1}{\tau}\right)_{\text{Jeans}} = \frac{80}{9} n \sqrt{\frac{kT}{\pi m}} \, \pi\sigma^2 \left(\frac{m\delta^2}{\Gamma}\right). \tag{6.4-1}$$

Comparing this with the result given in Eq. 6.1-8, we find that

$$\left(\frac{1}{\tau}\right)_{\text{Jeans}} = \frac{5}{3}\left(\frac{1}{\tau}\right)_{c.l.} \tag{6.4-2}$$

Thus his result differs from ours only by a factor of 5/3.

In order to compare our results with those which would be obtained using the Mason-Monchick[35] approximate formula for the coefficient of thermal conductivity, we compute the classical limit of a quantity D introduced by Mason and Monchick and called the self-diffusion coefficient, the formula for which is

$$\frac{1}{D} = \frac{8p}{3\sqrt{\pi m kT}} \left[\sum_{\bar{\ell}^a} (2\bar{\ell}^a+1) e^{-\epsilon_{\bar{\ell}^a}}\right]^{-2}$$

$$\times \sum_{\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b} (2\bar{\ell}^a+1)(2\bar{\ell}^b+1)\, e^{-\epsilon_{\bar{\ell}^a}-\epsilon_{\bar{\ell}^b}} \int \bar{\gamma}^5 e^{-\bar{\gamma}^2}$$

$$\times (1-\cos\chi)\, I(\bar{e}^a \bar{e}^b e^a e^b) \sin\chi \, d\chi \, d\varphi \, d\bar{\gamma} ,$$

(6.4-3)

where ρ is the mass density. When we compute the classical limit of this quantity we obtain

$$\left(\frac{1}{D}\right)_{c.l.} = \frac{8}{3} \rho \frac{\pi\sigma^2}{\sqrt{\pi m k T}} \left(1 - \frac{5}{18} \frac{m\delta^2}{\Gamma}\right) . \tag{6.4-4}$$

The Mason-Monchick approximation then consists of writing

$$Z \approx \frac{3}{2} \left(\frac{c^{(int)} T}{\rho D}\right) + \frac{3}{4} \left(\frac{C^{(int)}}{n k \tau}\right) , \tag{6.4-5}$$

where Z is the quantity given by Eq. 6.3-6. If we use our results for $(1/\tau)_{c.l.}$, Eq. 6.1-8, and $(1/D)_{c.l.}$, Eq. 6.4-4, we obtain

$$(Z)_{M.M.} = 4\sqrt{\frac{kT}{\pi m}}\,\pi\sigma^2\left(1+\frac{13}{18}\,\frac{m\delta^2}{I}\right). \qquad (6.4\text{-}6)$$

The classical limit of this quantity is given by Eq. 6.3-25.

In arriving at the expression in Eq. 6.4-5, Mason and Monchick make three approximations. In making the expansion of γ in powers of $\Delta\epsilon$, Eq. 6.3-19, they keep two terms. In the present development, the third term also contributes. The contribution to Z thereby neglected is

$$\frac{1}{2}\sqrt{\frac{kT}{\pi m}}\left[\sum_{\bar{l}^a}(2\bar{l}^a+1)e^{-\epsilon_{\bar{l}^a}}\right]^{-2}\sum_{\bar{l}^a\bar{l}^b l^a l^b}(\epsilon_{\bar{l}^a}-\langle\epsilon\rangle)$$

$$\times(\epsilon_{\bar{l}^a}-\epsilon_{\bar{l}^b})(2\bar{l}^a+1)(2\bar{l}^b+1)e^{-\epsilon_{\bar{l}^a}-\epsilon_{\bar{l}^b}}(\Delta\epsilon)^2$$

$$\times\int\bar{\gamma}e^{-\bar{\gamma}^2}\cos\chi\, I(\bar{l}^a\bar{l}^b l^a l^b)\sin\chi\, d\chi\, d\varphi\, d\bar{\gamma}.$$

$$(6.4\text{-}7)$$

The classical limit of the above expression is

$$-\frac{4}{9}\sqrt{\frac{kT}{\pi m}}\,\pi\sigma^2\left(\frac{m\delta^2}{I}\right). \qquad (6.4\text{-}8)$$

The second approximation was to neglect the quantity

$$-4\sqrt{\frac{kT}{\pi m}}\left[\sum_{\bar{l}^a}(2\bar{l}^a+1)\,e^{-\epsilon_{\bar{l}^a}}\right]^{-2}$$

$$\times\sum_{\bar{l}^a\bar{l}^b l^a l^b}\left(\epsilon_{\bar{l}^a}-\langle\epsilon\rangle\right)(2\bar{l}^a+1)(2\bar{l}^b+1)\,e^{-\epsilon_{\bar{l}^a}-\epsilon_{\bar{l}^b}}$$

$$\times\left(\Delta\epsilon_{\bar{l}^a}-\Delta\epsilon_{\bar{l}^b}\right)\int\bar{\gamma}^5 e^{-\bar{\gamma}^2}\cos\chi\;I(\bar{l}^a\bar{l}^b l^a l^b)$$

$$\times\sin\chi\,d\chi\,d\varphi\,d\bar{\gamma}. \qquad (6.4\text{-}9)$$

The classical limit of the above expression is

$$-\frac{16}{9}\sqrt{\frac{kT}{\pi m}}\;\pi\sigma^2\left(\frac{m\delta^2}{I}\right). \qquad (6.4\text{-}10)$$

Finally, they make the approximation that

$$Z_2=\frac{3}{2}\left(\frac{C^{(int)}T}{\rho D}\right), \qquad (6.4\text{-}11)$$

where Z_2 is the quantity defined by Eq. 6.3-12. The classical limit of the quantity on the right hand side of the above equation is

$$4 \sqrt{\frac{kT}{\pi m}}\ \pi \sigma^{2} \left(1 - \frac{5}{18}\ \frac{m\delta^{2}}{I}\right). \qquad (6.4\text{-}12)$$

The classical limit of Z_2 is given by Eq. 6.3-18.

In this thesis we have obtained exact quantum mechanical expressions for the transport coefficients of a gas of loaded spheres, through second order in δ, the displacement of the center of mass from the geometrical center. We have, in this chapter, obtained the classical limit of these quantities. A purely classical treatment of the transport coefficients for this model, using the Chapman-Enskog method, has been given in two papers by Dahler and Sather[14], and Sandler and Dahler[15]. Their results are valid for all values of δ. When their results are expanded in power series in δ, and the terms arising from the coupling of the linear and angular velocities in the expansion of the perturbation function are ignored, it is found that their results and those of the present treatment agree to terms in δ^2.

APPENDIX I

In this appendix we present a number of useful relations among representation coefficients, Wigner coefficients, and Racah coefficients. They are taken from Appendix A of the Thesis of George Gioumousis[38]; Tables of Racah Coefficients, by Simon, Vander Sluis, and Biedenharn[39]; and The Theory of Atomic Spectra, by Condon and Shortley[32].

Representation Coefficients and Integrals

$$\int f(R)\,dR = \int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} f(R)\sin\beta\, d\alpha\, d\beta\, d\gamma \;. \tag{A.1-1}$$

$$\int D^{\ell'}(R)^{*}_{n'm'}\, D^{\ell}(R)_{nm}\, dR = \delta_{\ell\ell'}\,\delta_{nn'}\,\delta_{mm'}\,\frac{8\pi^2}{2\ell+1} \;. \tag{A.1-2}$$

$$D^{\ell_1}(R)_{m_1 n_1}\, D^{\ell_2}(R)_{m_2 n_2} = \sum_{\ell_3} S^{\ell_1\ell_2}_{\ell_3 m_1 m_2}\, S^{\ell_1\ell_2}_{\ell_3 n_1 n_2}\, D^{\ell_3}(R)_{m_1+m_2,\, n_1+n_2} \;. \tag{A.1-3}$$

$$\int D^{\ell_3}(R)^{*}_{m_3 n_3}\, D^{\ell_1}(R)_{m_1 n_1}\, D^{\ell_2}(R)_{m_2 n_2}\, dR$$

$$= \frac{8\pi^2}{2\ell_3+1}\, S^{\ell_1\ell_2}_{\ell_3 m_1 m_2}\, S^{\ell_1\ell_2}_{\ell_3 n_1 n_2}\, \delta_{m_3,\, m_1+m_2}\, \delta_{n_3,\, n_1+n_2} \;. \tag{A.1-4}$$

Wigner Coefficients

$$\sum_{\alpha} S^{ab}_{c\alpha\gamma-\alpha} S^{ab}_{c'\alpha\gamma-\alpha} = \delta_{cc'} \Delta(abc), \qquad \text{(A.1-5)}$$

where

$$\begin{aligned} \Delta(abc) &= 1 \quad \text{for} \quad |a-c| \leq b \leq a+c, \\ &= 0 \quad \text{otherwise} \end{aligned}$$

$$\sum_{c} S^{ab}_{c\alpha\gamma-\alpha} S^{ab}_{c\alpha'\gamma-\alpha'} = \delta_{\alpha\alpha'}. \qquad \text{(A.1-6)}$$

$$\begin{aligned} S^{ab}_{c\alpha\beta} &= S^{ba}_{c-\beta-\alpha} = (-1)^{a+b-c} S^{ba}_{c\beta\alpha} \\ &= (-1)^{a+b-c} S^{ab}_{c-\alpha-\beta}. \end{aligned} \qquad \text{(A.1-7)}$$

$$S^{ab}_{c\alpha\beta} = (-1)^{a-\alpha} \sqrt{\frac{2c+1}{2b+1}} S^{ac}_{b,\alpha,-\alpha-\beta}. \qquad \text{(A.1-8)}$$

$$= (-1)^{b+\beta} \sqrt{\frac{2c+1}{2a+1}} S^{cb}_{a,-\alpha-\beta,\beta}. \qquad \text{(A.1-9)}$$

$$S^{a0}_{c2\beta} = \delta_{ac}\,\delta_{\beta 0}. \tag{A.1-10}$$

$$S^{eb}_{a\epsilon\beta}\, S^{ed}_{c-\epsilon\,\delta} = (-1)^{a+b+\epsilon}\sqrt{(2a+1)(2c+1)}$$

$$\times \sum_{f} S^{bd}_{f\beta\delta}\, S^{ac}_{f,-\beta-\epsilon,\epsilon-\delta}\, W(abcdef). \tag{A.1-11}$$

$$\sum_{e}(2e+1)(2f+1)\,W(abcdef)\,W(abcdeg) = \delta_{fg}\,\Delta(acf)\,\Delta(bdf). \tag{A.1-12}$$

$$\sqrt{(2b+1)(2c+1)}\,W(abcd0f) = (-1)^{b+c+f}\,\delta_{ab}\,\delta_{cd}\,\Delta(acf)\,\Delta(bdf) \tag{A.1-13}$$

$$\sum_{g}(2g+1)\,W(\bar{a}g\,be\,a\bar{e})\,W(cg\,d\bar{e}\,\bar{c}e)\,W(\bar{a}g\,fc\,a\bar{c})$$

$$= W(abcdef)\,W(\bar{a}b\bar{c}d\bar{e}f). \tag{A.1-14}$$

$$W(abcdef) = W(badcef) \tag{A.1-15}$$

$$= W(acbdfe) \tag{A.1-16}$$

$$= W(cdabef) \tag{A.1-17}$$

$$= (-1)^{e+f-a-d} \quad W(ebcfad) \tag{A.1-18}$$

$$= (-1)^{e+f-b-c} \quad W(aefdbc). \tag{A.1-19}$$

<u>Explicit Expressions for Certain Wigner Coefficients</u>

$$S^{\lambda 1}_{\lambda+1\,00} = \sqrt{\frac{\lambda+1}{2\lambda+1}} \tag{A.1-20}$$

$$S^{\lambda 1}_{\lambda-1\,00} = -\sqrt{\frac{\lambda}{2\lambda+1}} \qquad \text{(A.1-21)}$$

$$S^{\lambda 2}_{\lambda+2\,00} = \sqrt{\frac{3(\lambda+1)(\lambda+2)}{2(2\lambda+1)(2\lambda+3)}} \qquad \text{(A.1-22)}$$

$$S^{\lambda 2}_{\lambda\,00} = -\frac{\lambda(\lambda+1)}{\sqrt{(2\lambda-1)\lambda(\lambda+1)(2\lambda+3)}} \qquad \text{(A.1-23)}$$

$$S^{\lambda 2}_{\lambda+2\,00} = \sqrt{\frac{3\lambda(\lambda-1)}{2(2\lambda-1)(2\lambda+1)}} \qquad \text{(A.1-24)}$$

APPENDIX II

The following two identities are used frequently in this thesis,

$$\sum_{s\tau} S^{l,\bar{l}^{b}}_{l^{b}0\,\tau-s}\; S^{l^{a}l^{b}}_{l s\,\tau-s}\; S^{l^{a}\bar{l}^{b}}_{\bar{l} s\,\tau-s}\; S^{l\lambda}_{L\tau 0}\; S^{\bar{l}\bar{\lambda}}_{L\tau 0}$$

$$= (-1)^{l^{b}+\bar{l}^{b}+l,}\sqrt{\frac{(2l+1)(2l^{b}+1)(2\bar{l}+1)}{2\bar{\lambda}+1}}\,(2L+1)\; S^{l,\lambda}_{\bar{\lambda}00}$$

$$\times W(l,\bar{l}^{b} l l^{a} l^{b}\bar{l})\, W(\bar{l} l, L\lambda l\bar{\lambda}),$$

(A.2-1)

and

$$\sum_{s\tau} S^{l,\bar{l}^{a}}_{l^{a}0 s}\; S^{l^{a}l^{b}}_{l s\,\tau-s}\; S^{\bar{l}^{a}l^{b}}_{\bar{l} s\,\tau-s}\; S^{l\lambda}_{L\tau 0}\; S^{\bar{l}\bar{\lambda}}_{L\tau 0}$$

$$= (-1)^{l+\bar{l}+l,}\sqrt{\frac{(2l+1)(2l^{a}+1)(2\bar{l}+1)}{2\bar{\lambda}+1}}\,(2L+1)\; S^{l,\lambda}_{\bar{\lambda}00}$$

$$\times W(l,\bar{l}^{a} l l^{b} l^{a}\bar{l})\, W(\bar{l} l, L\lambda l\bar{\lambda}).$$

(A.2-2)

We give a derivation of the second of these identities.

Let P equal the quantity on the left hand side of Eq. A.2-2. From Eqs. A.1-9 and A.1-11 we have

$$S^{\ell_1 \bar{\ell}^a}_{\ell^a 0 s} \, S^{\ell^a \ell^b}_{\ell s \tau - s} = (-1)^{\bar{\ell}^a + s} \sqrt{\frac{2\ell^a+1}{2\ell_1+1}} \, S^{\ell^a \bar{\ell}^a}_{\ell_1 \, -s \, s} \, S^{\ell^a \ell^b}_{\ell s \tau - s}$$

$$= (-1)^{\ell_1} \sqrt{(2\ell^a+1)(2\ell+1)} \sum_f S^{\bar{\ell}^a \ell^b}_{f s \tau - s} \, S^{\ell_1 \ell}_{f 0 -\tau}$$

$$W(\ell_1 \bar{\ell}^a \ell \ell^b \ell^a f). \tag{A.2-3}$$

Upon carrying out the sum over s by means of Eq. A.1-5 we find

$$\sum_s S^{\ell_1 \bar{\ell}^a}_{\ell^a 0 s} \, S^{\ell^a \ell^b}_{\ell s \tau - s} \, S^{\bar{\ell}^a \ell^b}_{\bar{\ell} s \tau - s} = (-1)^{\ell_1} \sqrt{(2\ell+1)(2\ell^a+1)}$$

$$S^{\ell_1 \ell}_{\bar{\ell} 0 -\tau} \, W(\ell_1 \bar{\ell}^a \ell \ell^b \ell^a \bar{\ell}). \tag{A.2-4}$$

Also, by using Eqs. A.1-7 and A.1-11 we get

$$S^{l_1 l}_{\bar{l}0-\tau}\, S^{l\lambda}_{\bar{L}\tau 0} = (-1)^{l_1+l+\bar{l}}\, S^{l l_1}_{\bar{l}-\tau 0}\, S^{l\lambda}_{L\tau 0}$$

$$= (-1)^{l+\tau}\sqrt{(2\bar{l}+1)(2\bar{L}+1)}\ \sum_{f} S^{l_1\lambda}_{f00}\, S^{\bar{l}L}_{f\tau-\tau}$$

$$\times W(\bar{l}l, L\lambda l f). \tag{A.2-5}$$

But, by Eq. A.1-8,

$$S^{\bar{l}\bar{\lambda}}_{L\tau 0} = (-1)^{\bar{l}+\tau}\sqrt{\frac{2L+1}{2\bar{\lambda}+1}}\ S^{\bar{l}L}_{\bar{\lambda}\tau-\tau}. \tag{A.2-6}$$

Hence

$$P = (-1)^{l+\bar{l}+l_1}\sqrt{\frac{(2l+1)(2l^a+1)(2\bar{l}+1)}{2\bar{\lambda}+1}}\ (2L+1)$$

$$\times W(l_1\bar{l}^a l l^b l^a \bar{l}) \sum_{\tau f} S^{l_1\lambda}_{f00}\, S^{\bar{l}L}_{f\tau-\tau}\, S^{\bar{l}L}_{\bar{\lambda}\tau-\tau}$$

$$\times W(\bar{l}l, L\lambda l f). \tag{A.2-7}$$

We carry out the sums over τ and f by using Eq. A.1-5. The result given in Eq. A.2-2 then follows.

The derivation of Eq. A.2-1 is virtually identical.

APPENDIX III

The expression for $I_{inel}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | J)_2$, Eq. 3.4-4, may be written in the form

$$I_{inel}(\bar{\ell}^a \bar{\ell}^b \ell^a \ell^b | J)_2 = \frac{2J+1}{3\mathcal{H}\bar{\mathcal{H}}^3 \sigma^2}$$

$$\times \left\{ \left(S^{1\bar{\ell}^a}_{\ell^a 00} \right)^2 \delta_{\ell^b \bar{\ell}^b} + \left(S^{1\bar{\ell}^b}_{\ell^b 00} \right)^2 \delta_{\ell^a \bar{\ell}^a} \right\} \sum_{\lambda\lambda'\bar{\lambda}\bar{\lambda}'} F_J(\lambda\lambda'\bar{\lambda}\bar{\lambda}')$$

$$\times \frac{1}{h_\lambda(\mathcal{H}\sigma) h_{\bar{\lambda}}(\bar{\mathcal{H}}\sigma) h^*_{\lambda'}(\mathcal{H}\sigma) h^*_{\bar{\lambda}'}(\bar{\mathcal{H}}\sigma)} , \qquad \text{(A.3-1)}$$

where

$$F_J(\lambda\lambda'\bar{\lambda}\bar{\lambda}') = (-1)^{1+J+\lambda+\bar{\lambda}'} \, i^{\bar{\lambda}-\bar{\lambda}'+\lambda'-\lambda}$$

$$\times \sqrt{(2\lambda'+1)(2\bar{\lambda}+1)} (2\lambda+1) S^{\lambda J}_{\lambda' 00} S^{\bar{\lambda} J}_{\bar{\lambda}' 00} S^{\lambda 1}_{\bar{\lambda} 00} S^{\lambda' 1}_{\bar{\lambda}' 00}$$

$$\times W(\lambda \bar{\lambda} \lambda' \bar{\lambda}' 1 J). \qquad \text{(A.3-2)}$$

As we mentioned in Section 3.4, for any value of λ , the possible values of λ' , $\bar{\lambda}$, and $\bar{\lambda}'$ are restricted by the Wigner coefficients. For J equal to one, there are six combinations of these indices which lead to nonzero values of $F_J(\lambda\lambda'\bar{\lambda}\bar{\lambda}')$; for J equal to two, there are ten combinations. We list these in the following two tables.

Values of the Function $F_1(\lambda\lambda'\bar{\lambda}\bar{\lambda}')$

λ'	$\bar{\lambda}$	$\bar{\lambda}'$	$F_1(\lambda\lambda'\bar{\lambda}\bar{\lambda}')$
$\lambda+1$	$\lambda+1$	$\lambda+2$	$\frac{(\lambda+1)(\lambda+2)}{2\lambda+3}$
$\lambda+1$	$\lambda+1$	λ	$-\frac{\lambda+1}{(2\lambda+1)(2\lambda+3)}$
$\lambda+1$	$\lambda-1$	λ	$\frac{\lambda(\lambda+1)}{2\lambda+1}$
$\lambda-1$	$\lambda+1$	λ	$\frac{\lambda(\lambda+1)}{2\lambda+1}$
$\lambda-1$	$\lambda-1$	λ	$-\frac{\lambda}{(2\lambda-1)(2\lambda+1)}$
$\lambda-1$	$\lambda-1$	$\lambda-2$	$\frac{(\lambda-1)\lambda}{2\lambda-1}$

Values of the Function $F_2(\lambda\lambda'\bar{\lambda}\bar{\lambda}')$

λ'	$\bar{\lambda}$	$\bar{\lambda}'$	$F_2(\lambda\lambda'\bar{\lambda}\bar{\lambda}')$
λ	$\lambda+1$	$\lambda+1$	$\frac{\lambda(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)}$
λ	$\lambda-1$	$\lambda-1$	$\frac{(\lambda-1)\lambda(\lambda+1)}{(2\lambda-1)(2\lambda+1)}$
$\lambda-2$	$\lambda+1$	$\lambda-1$	$\frac{3}{2}\frac{(\lambda-1)\lambda(\lambda+1)}{(2\lambda-1)(2\lambda+1)}$
$\lambda-2$	$\lambda-1$	$\lambda-3$	$\frac{3}{2}\frac{(\lambda-2)(\lambda-1)\lambda}{(2\lambda-3)(2\lambda-1)}$
$\lambda+2$	$\lambda-1$	$\lambda+1$	$\frac{3}{2}\frac{\lambda(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)}$
$\lambda+2$	$\lambda+1$	$\lambda+3$	$\frac{3}{2}\frac{(\lambda+1)(\lambda+2)(\lambda+3)}{(2\lambda+3)(2\lambda+5)}$
$\lambda-2$	$\lambda-1$	$\lambda-1$	$-3\frac{(\lambda-1)\lambda}{(2\lambda-3)(2\lambda-1)(2\lambda+1)}$
λ	$\lambda-1$	$\lambda+1$	$-3\frac{\lambda(\lambda+1)}{(2\lambda-1)(2\lambda+1)(2\lambda+3)}$
λ	$\lambda+1$	$\lambda-1$	$-3\frac{\lambda(\lambda+1)}{(2\lambda-1)(2\lambda+1)(2\lambda+3)}$
$\lambda+2$	$\lambda+1$	$\lambda+1$	$-3\frac{(\lambda+1)(\lambda+2)}{(2\lambda+1)(2\lambda+3)(2\lambda+5)}$

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